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Dr. Valery Kuzmich Brel

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Institute of Physiologically Active Compounds
Severny proezd, 1
Chernogolovka, 142432
Russia

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14. ABSTRACT

This report results from a contract tasking Institute of Physiologically Active Compounds as follows: The contractor will investigate and develop new methods for introduction of pentafluorothio groups (SF5) into various unsaturated, heterocyclic and aromatic molecular systems and will synthesize new materials containing SF5-groups. The majority of synthesized materials (or composition) will be subjected to a broad spectrum of physics-chemical tests. Expected results include: a) synthesis and study of reactions homo- and copolymerization for new types of unsaturated compounds with pentafuorosulfanyl (SF5) groupings; b) new methods of introduction pentafluorothio groups (SF5) into various unsaturated, heterocyclic and aromatic molecular systems will be developed; c) study of reaction fluorination of ethers with pentafluorothio groups (SF5), nitro (NO2) groups and related compounds having electron-withdrawing groups.

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a. REPORT	b. ABSTRACT	c. THIS PAGE			SURYA SURAMPUDI
UNCLAS	UNCLAS	UNCLAS	UL	67	19b. TELEPHONE NUMBER *(Include area code)* +44 (0)20 7514 4299

ISTC 2791p

Final Project Technical Report
of ISTC 2791p

Development of the new approaches in designing of fluoroorganic derivatives of sulfur (unsaturated, heterocyclic, aromatic molecular systems and polyfunctional organic compounds)

(1 November 2003 - 31 October 2005, 24 months)

Valery Kuzmich Brel
(Project Manager)

Institute of Physiologically Active Compounds
Russian Academy of Sciences

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1. List of contents

2. Introduction

The project “Development of the new approaches in designing of fluoroorganic derivatives of sulfur (unsaturated, heterocyclic, aromatic molecular systems and polyfunctional organic compounds)” is the scientific investigation in the area of organic chemistry with the aim of construction of new pentafluorosulfanyl-containing organic compounds as well as the investigation of their spectral and physico-chemical properties. The project consists of three main stages: **Stage 1.** The preparation of new unsaturated compounds with pentafluorosulfanyl substituent and investigation of their properties; **Stage 2.** The study of Diels-Alder reactions and 1,3-dipolar cycloadditions of unsaturated compounds consisting of pentafluorosulfanyl moiety as well as fluorination reactions of ethers and esters containing electron-withdrawing groups by fluorine, xenon difluoride and electrophilic fluorinating agents $R_2N\text{-}F$, $[R_3N\text{-}F]^+ A^-$; **Stage 3.** The investigation of pentafluorosulfanylation of different unsaturated, aromatic and heterocyclic systems.

3. Method, Experiments.

The project ISTC 2791 is connected with basic researches and is directed on development of organic synthesis and on creation of new types of materials and compositions. In the framework of the project were received the following results: were developed a convenient method for preparation of organic compounds containing pentafluorosulfanyl substituent based on the photochemical addition of pentafluorosulfanyl chloride to different dienes and unsaturated alcohols. For the first time, were synthesized pentafluorosulfanyl-containing derivatives of 1,3-, 1,4-, and 1,5-dienes what are the promising monomers for the development of new polymer materials. It was shown that treatment with H_2O_2 leads to polymerization of 1-(pentafluorosulfanyl)-1,3-butadiene polymerizes with formation of some oligomers. Epoxidation of alkenes and dienes containing pentafluorosulfanyl group by m-chloroperoxybenzoic acid (mCPBA) has been studied. It was found that F_5S group deactivates double bond *vs* electrophilic reagents; double bonds connected directly to F_5S group are inert against mCPBA. For the first time, were synthesized active pentafluorosulfanyl-containing dienophiles using unsaturated alcohols as starting compounds. [2+4]-Cycloaddition reactions between these dienophiles and cyclopentadiene or electron-releasing acyclic 1,3-dienes have been

studied. Factors controlling the efficiency of this kinf of cycloaddition have been determined. Some new promising norbornene-based monomers with F_5S group for preparation of transparent polymers for 157 nm technology have been synthesized. Investigation of their polymerization is in progress now. Photo-induced radical addition of pentafluorosulfanyl chloride to esters of perfluoroacrylic acid has been studied. A new method of preparation of pentafluorosulfanyl-containing derivatives of perfluoropropionic acid has been developed. Reactions of F_5S-substituted alkenes and dienes with nitrile oxides have been investigated. For the first time, convenient method of preparation of 4,5-dihydroisoxazoles with pentafluorosulfanyl substituent has been developed. It was shown that 1-(pentafluorosulfanyl)-3-chloroprop-1-ene undergoes prototropic rearrangement in the presence of base. During the project realization for the first time we have synthesized 64 new compounds with pentafluorosulfanyl group. The structures of all synthesized compounds have been proved by ^{1}H, ^{19}F, and ^{13}C spectroscopy data.

4. Results

Compounds containing pentafluorosulfanyl group are receiving much attention due to advantageous properties of SF_5 substituent such as high electronegativity value, large steric demands, thermal and hydrolytic stability, *etc*. Besides, because high radiative and chemical stability of pentafluorosulfanyl group these substances are an attractive replacements for compounds that contain a trifluoromethyl group. These new properties are manifested in a multitude of uses, or potential uses, such as fumigants, perfluorinated blood substituents, thermally and chemically stable systems in different applications,[1] energetic materials,[2] rocket fuels,[3] polymeric materials[4] and liquid crystals.[5]

According to the research plan of project 2791p, four main directions of our investigations were realized during 24 months:

- Synthesis of unsaturated compounds containing pentafluorosulfanyl (F_5S-) fragment as perspective monomers for preparation of polymeric materials;
- Synthesis of heterocyclic compounds with F_5S-substituent.
- Investigation of reactivity of allylic systems containing pentafluorosulfanyl (F_5S-) fragment.
- Exploring the fluorination of ethers and acetals.

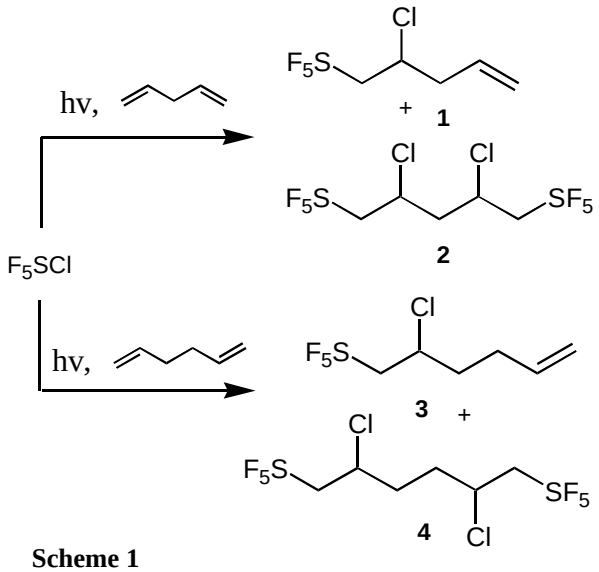
5. Synthesis of unsaturated compounds containing pentafluorosulfanyl (F_5S-) fragment as perspective monomers for preparation of polymeric materials

- Synthesis of perspective monomers from dienes with pentafluorosulfanyl (F_5S-) fragment

One of the most promising methods of preparation of pentafluorosulfanyl-containing compounds is pentafluorosulfanylation of unsaturated substrates.[6] To the start of this work, syntheses of some compounds with pentafluorosulfanyl group have been reported.[7] At the same time, the preparation of F_5S-substituted dienes with terminal CH_2-group, to the best of our knowledge, has not been described hitherto. Therefore, we have developed a convenient approach to the synthesis of pentafluorosulfanyl-containing 1,3-, 1,4- and 1,5-alkadienes and studied their reactivity.

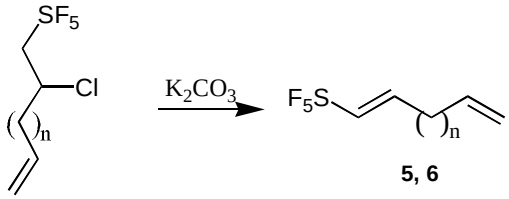
The same two-step approach has been used for preparation of 1-pentafluorosulfanylpenta-1,4-diene **5** and 1-pentafluorosulfanylhexa-1,5-diene **6**. In both cases, the first step is the photo-induced radical addition of pentafluorosulfanyl chloride to the corresponding 1,4- or 1,5-diene with

the formation of adducts **1** and **3**, respectively (Scheme 1). These reactions were performed at room temperature in a quartz ampoule using Hg lamp as a source of irradiation. Bis-adducts **2** and **4** are formed as by-products in the yields of 10-15% when F_5SCl reacts with 1,4- and 1,5-dienes, respectively. Products **1** – **4** have been isolated by vacuum distillation. Their structures have been unambigously proved by ^{1}H, ^{19}F and ^{13}C NMR spectroscopy. All products are formed by attack of F_5S radical on terminal carbon atom, *i.e.*, the studied photochemical reactions are completely regioselective.



Scheme 1

The second step of the preparation of alkadienes **5** and **6** is dehydrochlorination of monoadducts **1** and **3,** respectively, by treatment of their sulfolane solutions with K_2CO_3 at 60 ºC for 3 h (Scheme 2). The extent of reaction was monitored using thin-layer chromatography. It was found that the formation of 1-pentafluorosulfanylhexa-1,5-diene **6** is straightforward. On the contrary, elimination leading to 1-pentafluorosulfanylpenta-1,4-diene **5** is accompanied by partial isomerization of product into 1-pentafluorosulfanylpenta-2,4-diene. The extent of this isomerization has been found to increase with temperature. Therefore, we applied different procedures to isolation of 1,4-pentadiene **5** and 1,5-hexadiene **6**. Thermally stable product **6** was isolated by simple distillation at reduced pressure. Oppositely, prone to isomerization product **5** has been purified by column chromatography on silica gel.

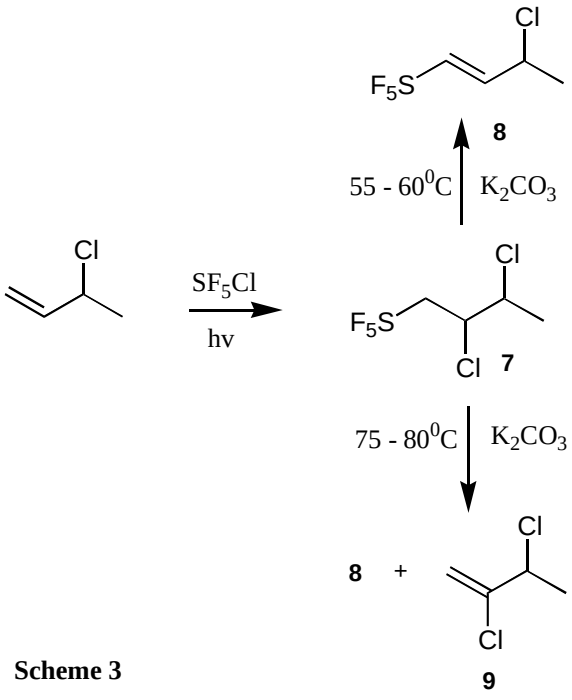


1,3 **5, 6**

n = 1 (**1**, **5**), 2 (**3**, **6**)

Scheme 2

We have tried to apply a similar two-step approach based on photochemical addition of F_5SCl to unsaturated substrate followed by HCl elimination for the synthesis of 1-pentafluorosulfanylbuta-1,3-diene. As unsaturated substrate we decided to used 3-chlorobut-1-ene. Indeed, adduct **7** is formed at above conditions with a good yield. It has been isolated in pure form by vacuum distillation. Unfortunately, transformation of formed adduct into the goal diene by K_2CO_3-induced elimination of two molecules of hydrogen chloride fails in studied solvents (DMF, sulfolane, *etc*.). Instead of diene, two allyl chlorides have been formed depending on reaction conditions. Heating at 55-60°C leads to elimination of one HCl mole with formation of 3-chloro-1-pentafluorosulfanylbut-1-ene **8**. It is stable at these conditions; second HCl molecule doesn't eliminate with the increase of reaction time.

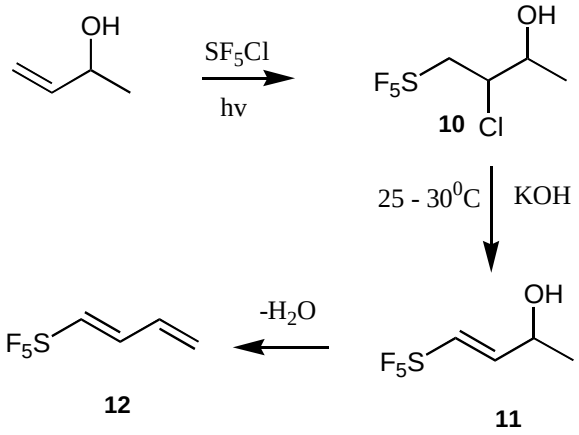


Scheme 3

Dehydrochlorination of **7** at higher temperature (75-80ºC) yielded the mixture of **8** and 2,3-dichlorobut-1-ene **9** in the ratio of 2:1 (Scheme 3).

Dichloride **9** is formed by HSF_5 elimination from adduct **7**. It means that at these conditions F_5S group behaves as a pseudohalide and competes with the chlorine atom in a base-induced elimination reaction. This is unexpected result because up to this study treatment of alkyl halides containing a F_5S group with bases led to elimination of hydrogen halide only but not HSF_5. The formation of **9** can be explained by the increased acidity of H(2) atom in 2,3-dichloro-1-pentafluorosulfanylbutane **7** due to inductive effects of electron-withdrawing substituents at both C(1) and C(3) atoms as well as by entropy factors. So, dehydrochlorination of **7** at 55-60ºC leads to elimination of one HCl molecule. Increase of reaction temperature to 80ºC gives rise to competition between the same dehydrochlorination and elimination of HSF_5. As H(4) atom is much less acidic, 1-pentafluorosulfanylbuta-1,3-diene is not obtained at these conditions.

Therefore, we have used another approach to the synthesis of 1-pentafluorosulfanylbuta-1,3-diene. But-3-en-2-ol reacts with F_5SCl under irradiation to yield adduct **10**. Treatment of compound **10** with KOH in diethyl ether affords allyl alcohol **11**. The reaction is mild and relatively fast; full conversion of **10** required 3 h at 25-30ºC.

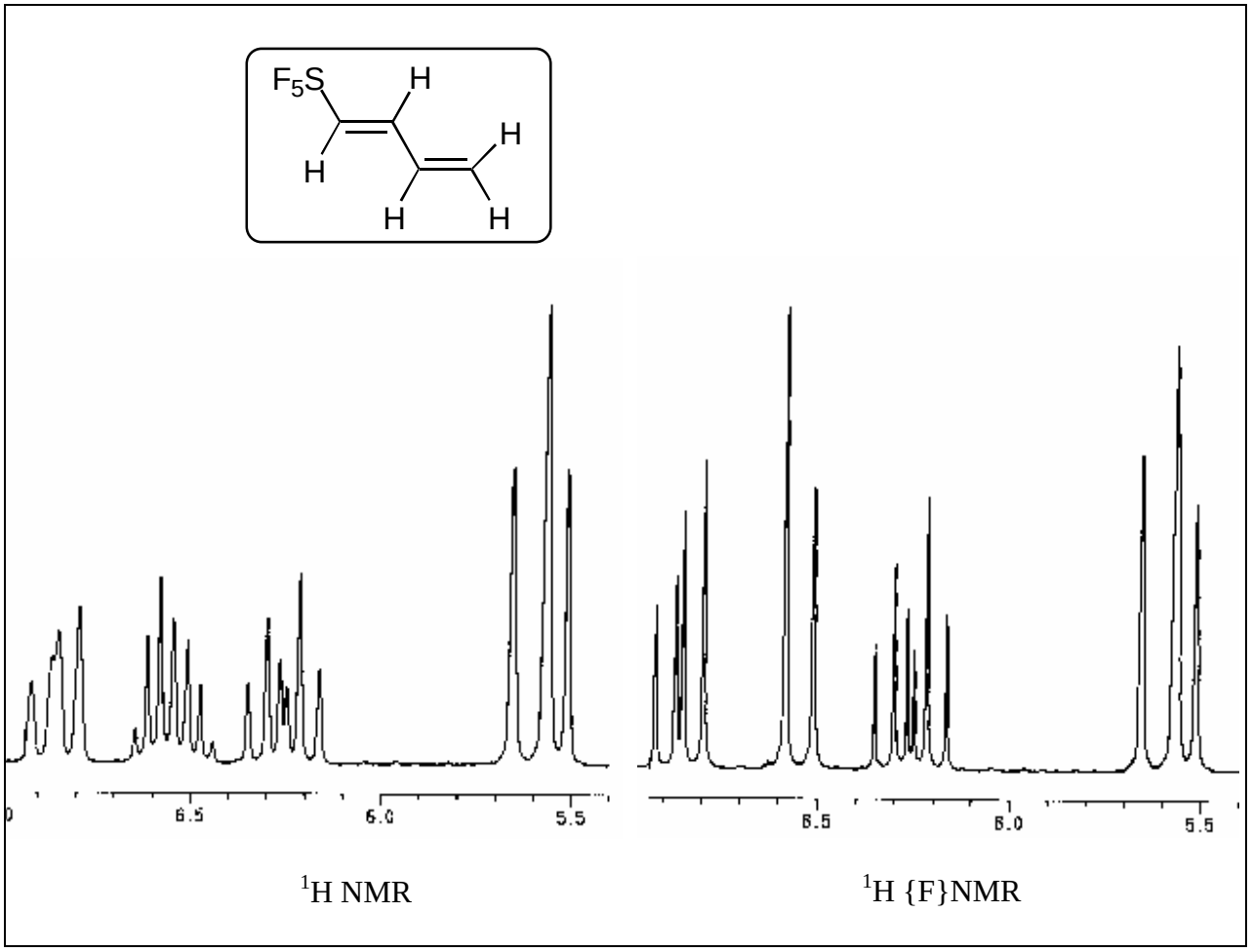


Scheme 4

Unsaturated alcohol **11** has been isolated by vacuum distillation. Exclusive formation of the *trans*-isomer in this elimination has been proved by ^{1}H, ^{19}F and ^{13}C NMR spectroscopy. The final step of synthesis of 1-pentafluorosulfanylbuta-1,3-diene **12** was dehydration of alcohol **11**. We have found that increase of the yield of **12** can be achieved by removal of product from reaction mixture.

So, reaction was performed under reduced pressure with simultaneous distillation of formed diene into a cooled trap. This procedure provided 1-pentafluorosulfanylbuta-1,3-diene with 35-40 % yield.

The structures of 1-pentafluorosulfanylhexa-1,5-diene **6**, 1-pentafluorosulfanylpenta-1,4-diene **5**, and 1-pentafluorosulfanylbuta-1,3-diene **12** have been unambiguously proved using ^{1}H, ^{19}F and ^{13}C NMR spectroscopy.

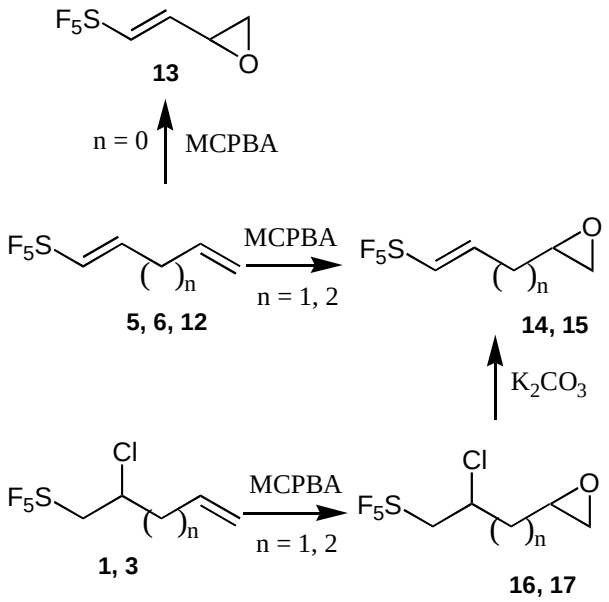


^{1}H NMR ^{1}H {F}NMR

The most useful method for this goal is ^{13}C NMR spectroscopy. The coupling constants J_{CF} of carbon atom connected directly to F_5S group as well as J_{CF} of atom C(2) are characteristic to the compounds containing pentafluorosulfanyl substituent. Thus, for **12** $\delta_{C(1)}$ = 141.74 ppm, doublet of pentets, J_{CF} = 1.6 and 20.4 Hz; $\delta_{C(2)}$ = 136.62 ppm, pentet, J_{CF} = 7.5 Hz. Siganls for C(3) and C(4) are singlets; their chemical shifts are the following: $\delta_{C(3)}$ = 131.35 and $\delta_{C(4)}$ = 126.54. The ^{19}F NMR spectra for compounds **5**, **6** and **12** showed no significant deviations from the chemical shifts or coupling constants found for other unsaturated derivatives of sulfur hexafluoride. The chemical

shifts of the apical fluorine atom in the SF_5-group were in the range of 140-141 ppm while the basal fluorines were observed at 160-161 ppm with the characteristic splitting due to AB_4-spin system (J_{AB} = 144-151 Hz).

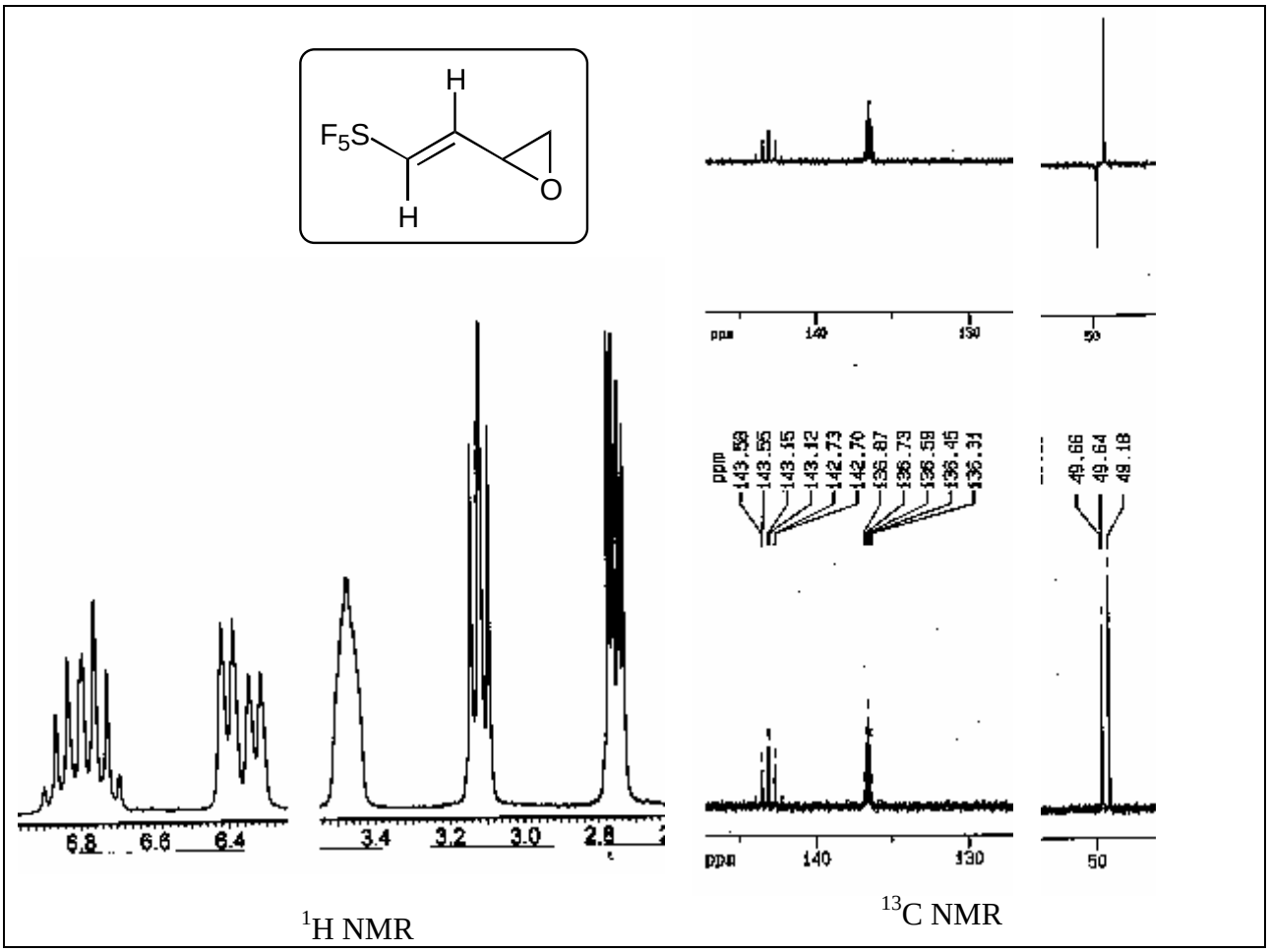
We have studied the epoxidation of F_5S-containing unsaturated compounds **5**, **6** and **12** by *meta*-chloroperoxybenzoic acid.[8] After 72 h these dienes were converted into monoepoxides **13** – **15** in the yields of 80-90% (Scheme 5). Epoxides **14** and **15** were also synthesized from adducts **1** and **3** by a two-step procedure. In the first step, these chloroalkenes were epoxidized with *meta*-chloroperoxybenzoic acid; the second step is HCl elimination from the obtained chloroalkyl epoxides **16** and **17**.



n = 0 (**12**) , 1 (**1**, **5**, **14**, **16**), 2 (**3**, **6**, **15**, **17**)

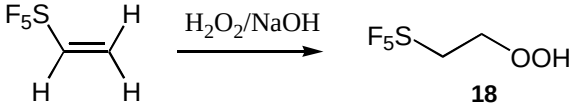
Scheme 5

For all substrates, unsubstituted terminal double bond is epoxidized exclusively. Oppositely, double bond connected to F_5S group doesn't react with electrophilic oxidant. These results can be explained by significant steric and electron-withdrawing effects of pentafluorosulfanyl groups. The structures of epoxides **13** – **15** have been proved by ^1H, ^{19}F and ^{13}C NMR spectroscopy.



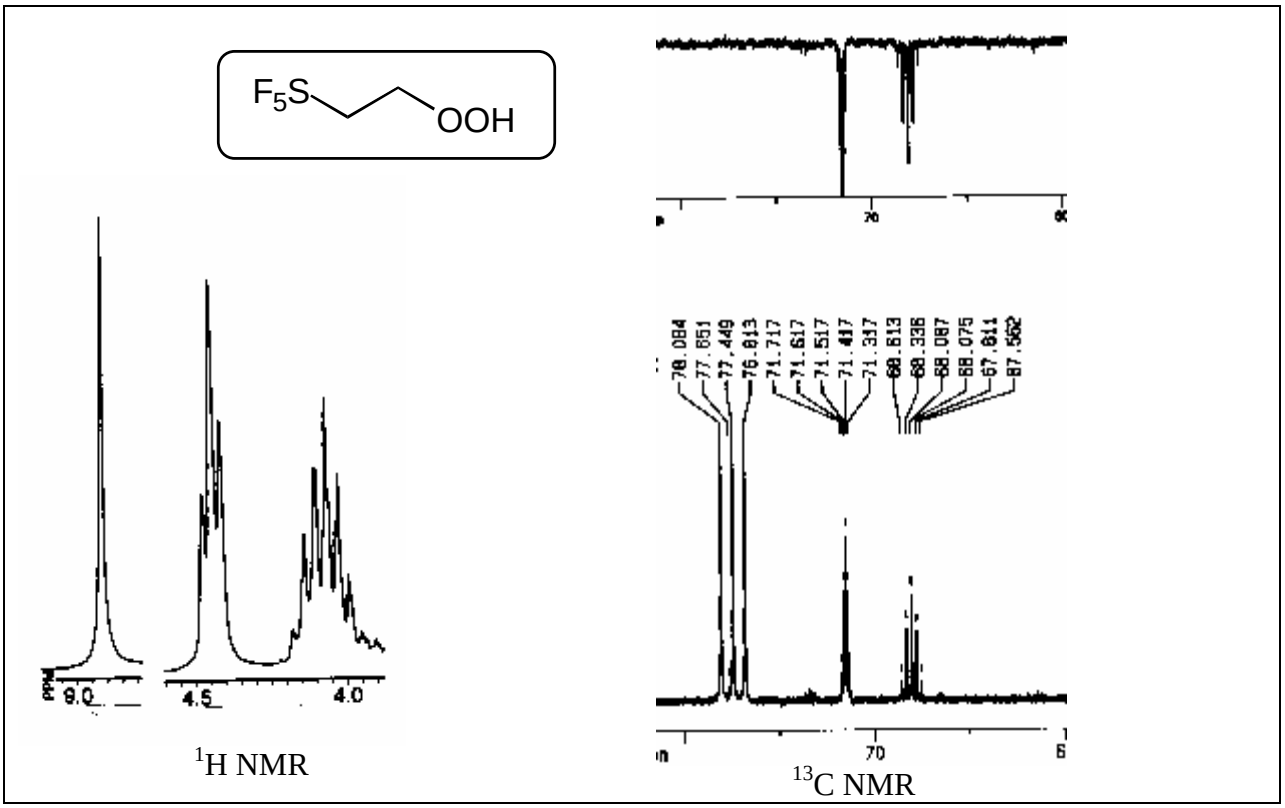
^{1}H NMR ^{13}C NMR

Then we decided to synthesize pentafluorosulfanylethylene oxide. So, we investigated oxidation of $F_5SCH=CH_2$ at various conditions. It was found that oxidation of double bound in $F_5SCH=CH_2$ is very difficult. Indeed, *meta*-chloroperoxybenzoic acid oxidized efficiently dienes **5, 6, 12** and alkenes **1, 3** but doesn't react with pentafluorosulfanylethene. At the same time, $F_5SCH=CH_2$ is oxidized by 30% alkaline solution of hydrogen peroxide. Product is formed in satisfactory yiled, however, it is not epoxide but hydroperoxide **18** (Scheme 6).



18

Scheme 6

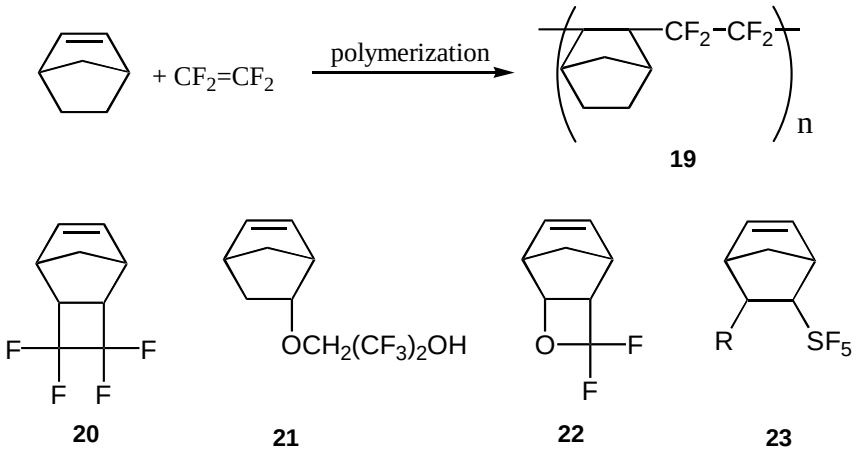


^{1}H NMR ^{13}C NMR

In summary, we have described an easy and convenient method for the preparation of new, synthetically valuable monomers with pentafluoro-λ^6-sulfanyl (SF_5) groups. 1-(Pentafluoro-λ^6-sulfanyl)-1,3-butadiene was transferred for study of the polymerization reaction to Laboratory de chimie macromoleculaire, Ecole Nationale Superieure de Chimie de Montpellier.

- Synthesis of perspective norbornene monomers on the base of unsaturated F_5S-derivatives for preparation of polymer materials

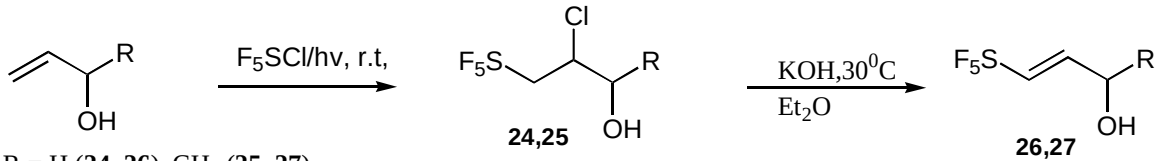
Among the most important demands to semiconductors are reduction of circuit size and increase of processor speed. It is why semiconductor industry has focused on extending the life of optical lithography using 157 nm technology.[9] One of the biggest challenges in this area has come in the photoresist. Because many organic compounds are opaque at 157 nm, designing transparent photoresists at this wavelength has become a challenging task. The most interesting materials **19** were synthesized using norbornene-based monomers **(**Scheme 7**)**. Furthermore, it was shown that introduction of bulky electron-withdrawing substituents to norbornene moiety raises a transparency of polymeric materials (Scheme 7, compounds **20 – 22**).[10]



Scheme 7

As pentafluorosulfanyl group has both large steric demands and large electronegativity value,[11] it can be interesting to construct the new monomers on the base of F_5S-substituted norbornenes. So, we decided to develop the approaches to synthesis of such norbornenes (for example, compounds **23** on Scheme 7). These norbornenes can be obtained, for example, by [4+2]-cycloaddition reaction between cyclopentadiene and F_5S-containing dienophiles. Unfortunately, to the start of our investigations, a single described pentafluorosulfanyl-substituted dienophile active in Diels-Alder reaction was pentafluorosulfanylacetylene. Oppositely, pentafluorosulfanylethylene fails cycloadd to dienes. So, we have developed the common method of synthesis of different dienophiles containing both F_5S-group and another electron-withdrawing substituent.

We have prepared such dienophiles from 1-pentafluorosulfanylprop-1-en-3-ol **26** and 1-pentafluorosulfanylbut-1-en-3-ol **27**. Precursors **26** and **27** have been synthesized by two-step procedures. In both cases, the first step is the photo-induced radical addition of pentafluorosulfanyl chloride to the corresponding allyl alcohols. Dehydrochlorination of formed adducts **24** and **25** with KOH gave **26** and **27** (Scheme 8).

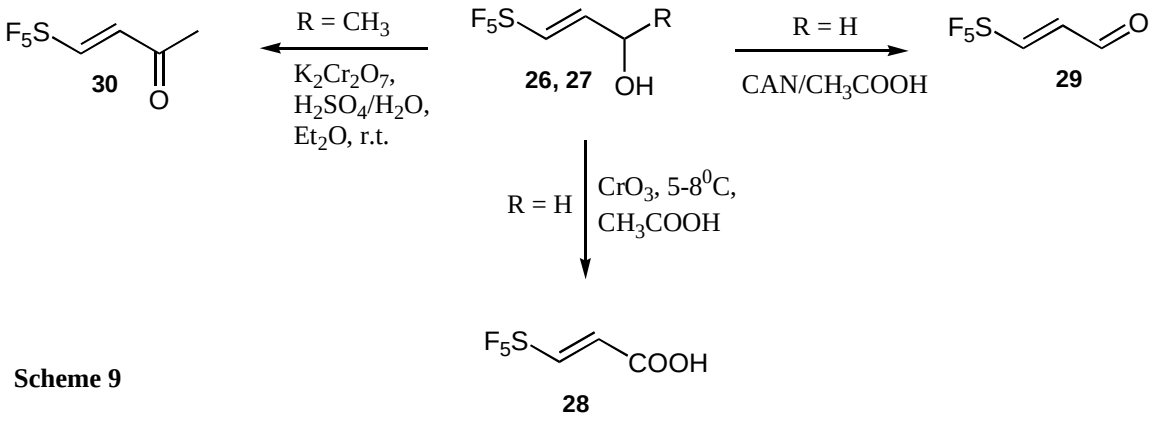


R = H (**24, 26**), CH_3 (**25, 27**).

Scheme 8

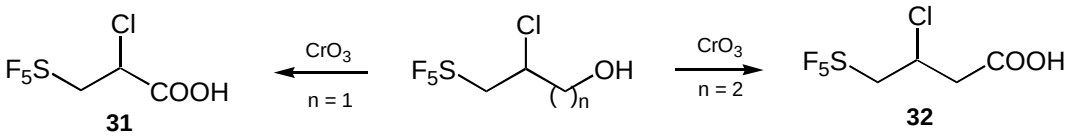
The primary alcohol **26** was oxidized by chromium trioxide[12] to afford acid **28** (Scheme 9). It has been purified by low-pressure distillation giving stable white solid (mp 74°C) in 60% yield.

Treatment of **26** with ceric ammonium nitrate (CAN) in aqueous acetic acid leads to aldehyde **29** with a satisfactory yield. Oxidation of secondary alcohol **27** by potassium dichromate in sulfuric acid provides the ketone **30** in a yield of 56% (Scheme 9).



Scheme 9

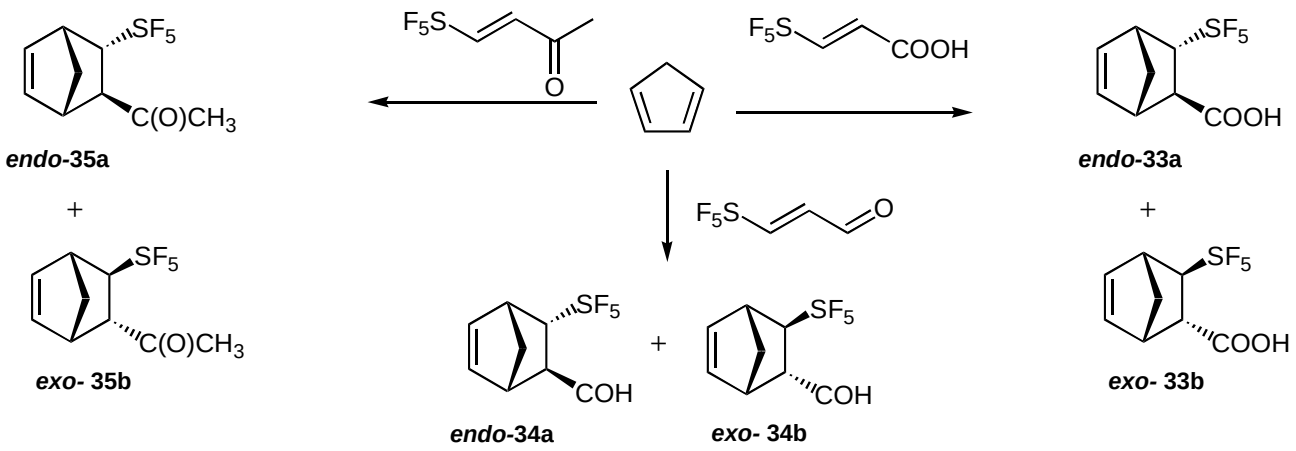
Similarly, oxidation of alcohols $F_5SCH_2CHClCH_2OH$ and $F_5SCH_2CHClCH_2CH_2OH$ by CrO_3 gave acids **31** and **32**, respectively, in a good yield (Scheme 10).



Scheme 10

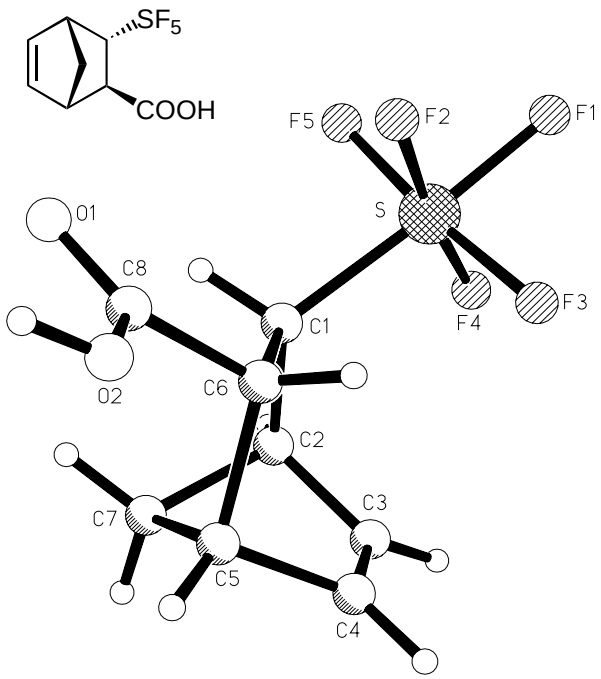
We have found that ketone **30** is less stable than acid **28**. In spite of it can be isolated in pure form by vacuum distillation ketone **30** slowly decomposes at keeping at room temperature. The structures of compounds **28 - 30** have been proved by ^{1}H, ^{19}F and ^{13}C NMR spectroscopy.

We have found that compounds **28 - 30** react readily with both aliphatic and cyclic electron-releasing dienes with the formation of the corresponding F_5S-containing Diels-Alder cycloadducts. The reactions were performed under nitrogen atmosphere in sealed glass tubes using 10 equiv of cyclopentadiene. In the case of acid **28** reaction finished after 48 h at room temperature but may be significantly accelerated by heating to 110°C (2h). The corresponding Diels-Alder cycloadditions of aldehyde **29** and ketone **30** proceed at 60°C (Scheme 11).

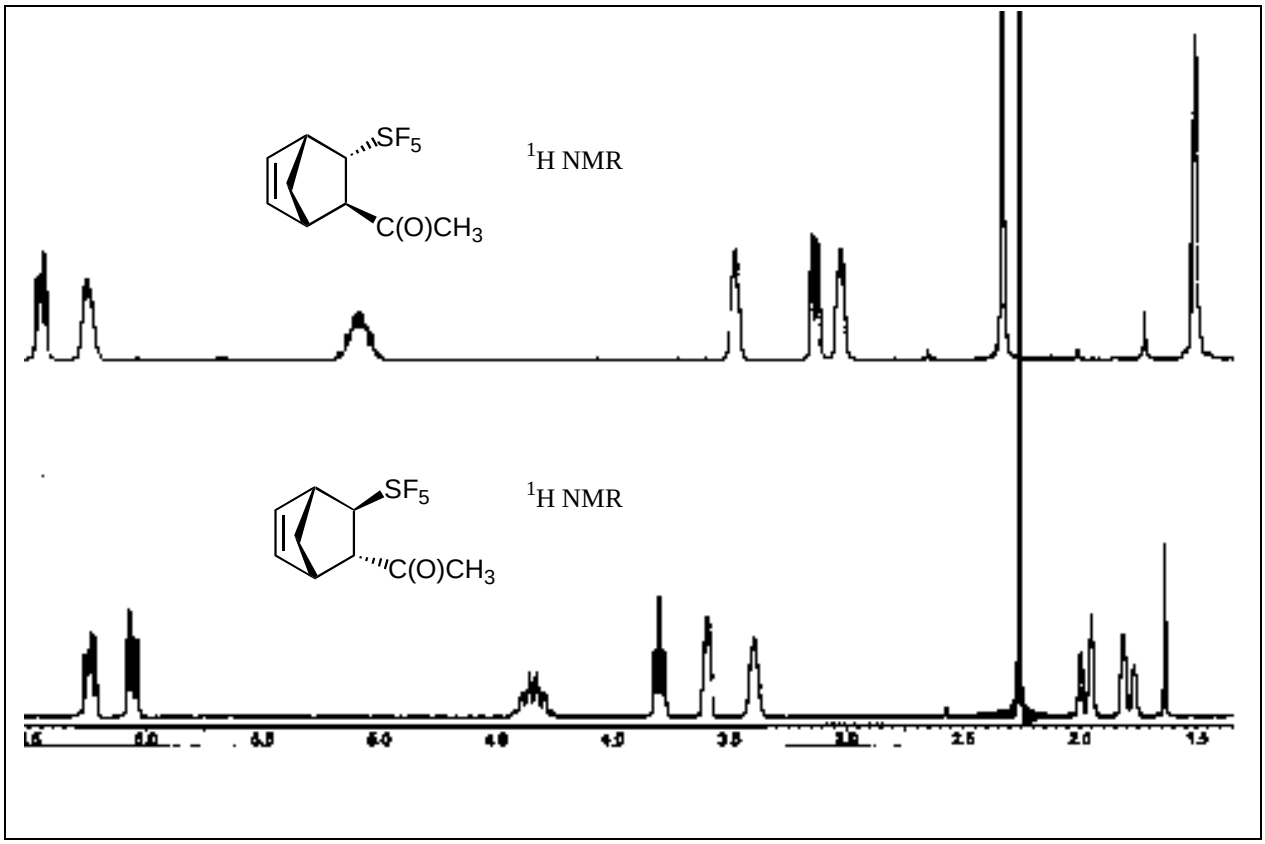


Scheme 11

After the time of reaction, ^{1}H NMR analysis of the reaction mixture revealed unchanged starting cyclopentadiene, dimer of cyclopentadiene and new compounds **33 - 35**. All of them are formed as a mixture of *endo*- and *exo*-isomers in *ca.* 3:1 ratio (Scheme 11). *Endo*-adducts **33a - 35a** and *exo*-adducts **33b - 35b** were isolated from reaction mixtures in pure form by preparative column chromatography.

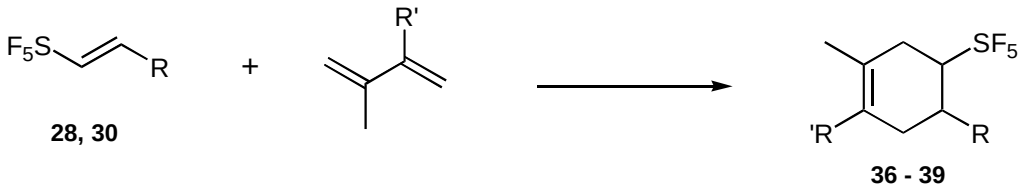


The structures of formed Diels-Alder cycloadducts were determined by ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy. For example, ^{1}H NMR spectra consist of characteristic signals of methine protons at 5.0 (*endo*-SF_5) and 4.2 (*exo*-SF_5) ppm. These appear as well-defined quintets. It demonstrates that coupling to four equatorial fluorine atoms of F_5S group is single important spin-spin interaction for these protons.



Analogously, coupling to fluorine atoms is manifested in ^{13}C NMR spectra. Thus, tertiary carbon atoms connecting with carbonyl group appeared in ^{13}C NMR spectra as quintets; signals of tertiary carbon atoms attached to pentafluorosulfanyl group are doublets of quintets. The ^{19}F NMR spectra for adducts **33** - **35** are very similar to those for other aliphatic derivatives of sulfur hexafluoride.[13] The chemical shifts of the apical fluorine atom in SF_5 group were in the range of 164-165 ppm while signals of basal fluorine atoms were observed at 139-140 ppm with the characteristic splitting due to AB_4-spim system, $J_{A\text{-}B}$ = 145-150 Hz.[14] The chemical shift of the four equatorial fluorine atoms of F_5S group is around 152 ppm. The structures of the synthesized cycloadducts **33** were unambiguously confirmed by single-crystal X-ray investigation of *endo*-isomer **33a**.

Reactions of compounds **28** and **29** with 2,3-dimethylbutadiene and 2-methylbutadiene led to the corresponding cycloadducts **36** - **39** (Scheme 12).

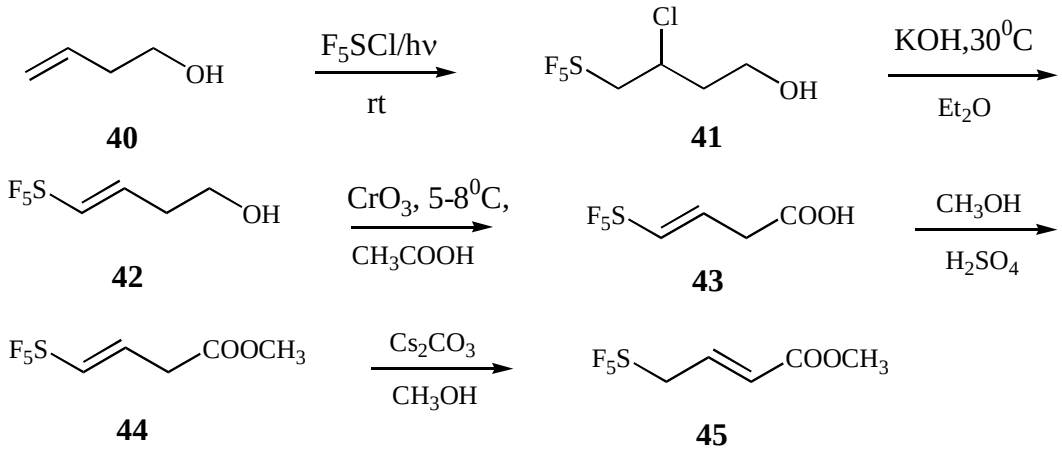


R = COOH, R' = CH_3 (**36**); R = COOH, R' = H (**37**); R = C(O)Me, R' = CH_3 (**38**); R = C(O)Me, R' = H (**39**)..

Scheme 12

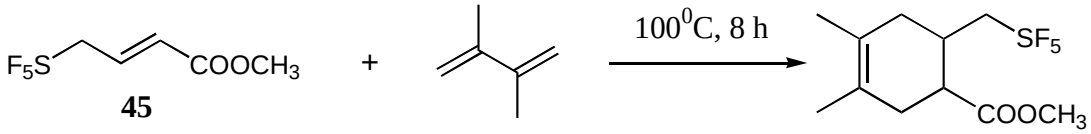
[4+2]-Cycloadditions of compounds **28 - 30** to cyclopentadiene, 2-methylbutadiene and 2,3-dimethylbutadiene yield the cycloadducts with pentafluorosulfanyl group attached directly to six-membered ring. We have also prepared cycloadducts wherein F_5S group is connected to ring by a short spacer. For realization of this goal, we have prepared methyl 4-(pentafluorosulfanyl)but-2-enoate **45** and studied its reactivity in Diels-Alder reaction.

As a starting compound for the synthesis of **45** we have used unsaturated alcohol **40** (Scheme 13). Analogously to above two-step procedure, this alcohol has been transformed into 1-(pentafluorosulfanyl)but-1-en-4-ol **42**. This alcohol has been oxidized by chromium trioxide in acetic acid into β,γ-unsaturated acid **43**. Its transformation into methyl ester was performed by standard esterification method. Stable ester **44** was purified by vacuum distillation. The last step of this synthesis is prototropic rearrangement what has been found by us in reactions of 1-(pentafluorosulfanyl)-3-chloroprop-1-ene (see below). Ester **44** smoothly rearranges into α,β-unsaturated ester **45** under treatment with methanolic cesium carbonate. The yield of **45** is 76%.



Scheme 13

Heating ester **45** with 2,3-dimethylbutadiene in sealed tube at 100°C for 8 h leads to cycloadduct **46** (Scheme 14). Compound **46** was isolated by column chromatography. Its structure has been proved by ^{1}H, ^{13}C and ^{19}F NMR spectroscopy data.



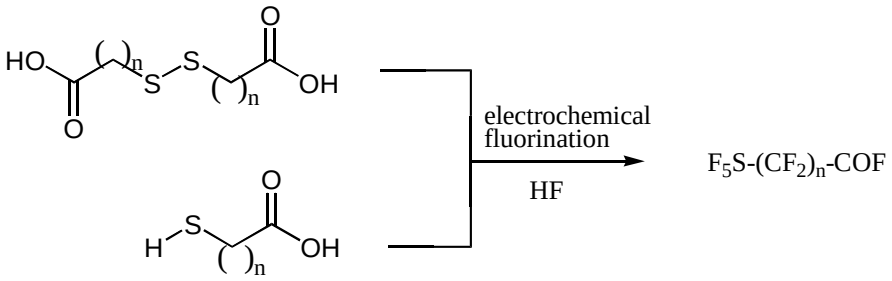
45 **46**

Scheme 14

In conclusion, we have developed a simple and efficient synthesis of novel pentafluorosulfanyl-containing dienophiles and have studied their reactions with cyclic and aliphatic electron-releasing dienes. Further application of this methodology to the synthesis of potentially interesting pentafluorosulfanyl-substituted compounds as well as the exploration of their properties will be studied. We have transferred compound **33** for study of its polymerization to professor W.R.Dolbier, Department of Chemistry, University of Florida.

6. Addition of F_5S radical to perfluoroacrylic acid derivatives. Synthesis of methyl 2,2,3,3-tetrafluoro-3-pentafluorosulfanylpropionate $F_5SCF_2CF_2COOMe$ and 2,2,3,3-tetrafluoro-3-pentafluorosulfanylpropanol $F_5SCF_2CF_2CH_2OH$

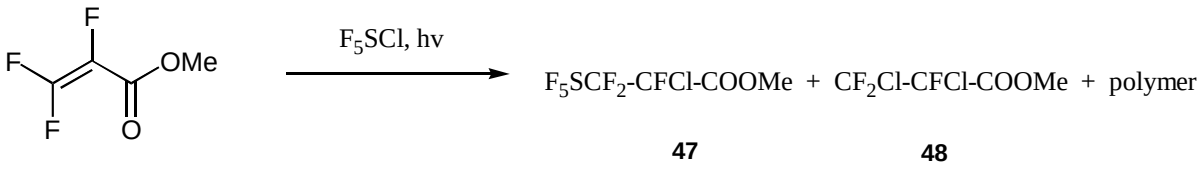
Recently organic compounds containing ω-(pentafluorosulfanyl)perfluoroalkyl (F_5SR_f) group have been received much attention. Due to high polarity these are applied in the development of new kinds of liquid crystals,[5] polymers[15] and synthetic materials with increased chemical, thermal and hydrolytic stability. Usually synthesis of F_5SR_f derivatives is based on the transformation of acids $F_5S(CF_2)_nCOOH$ as well as their derivatives: esters, amides, acyl fluorides. These acids are usually synthesized by electrochemical fluorination of carboxyalkyl mercaptans or the corresponding disulfides in liquid hydrogen fluoride (Scheme 15). Now it is industrial method what is using by different companies for the synthesis of $F_5S(CF_2)_nCOOH$.[16] Unfortunately, this approach is not applicable in laboratory due to necessity to use very expensive equipment and toxic hydrogen fluoride.



Scheme 15

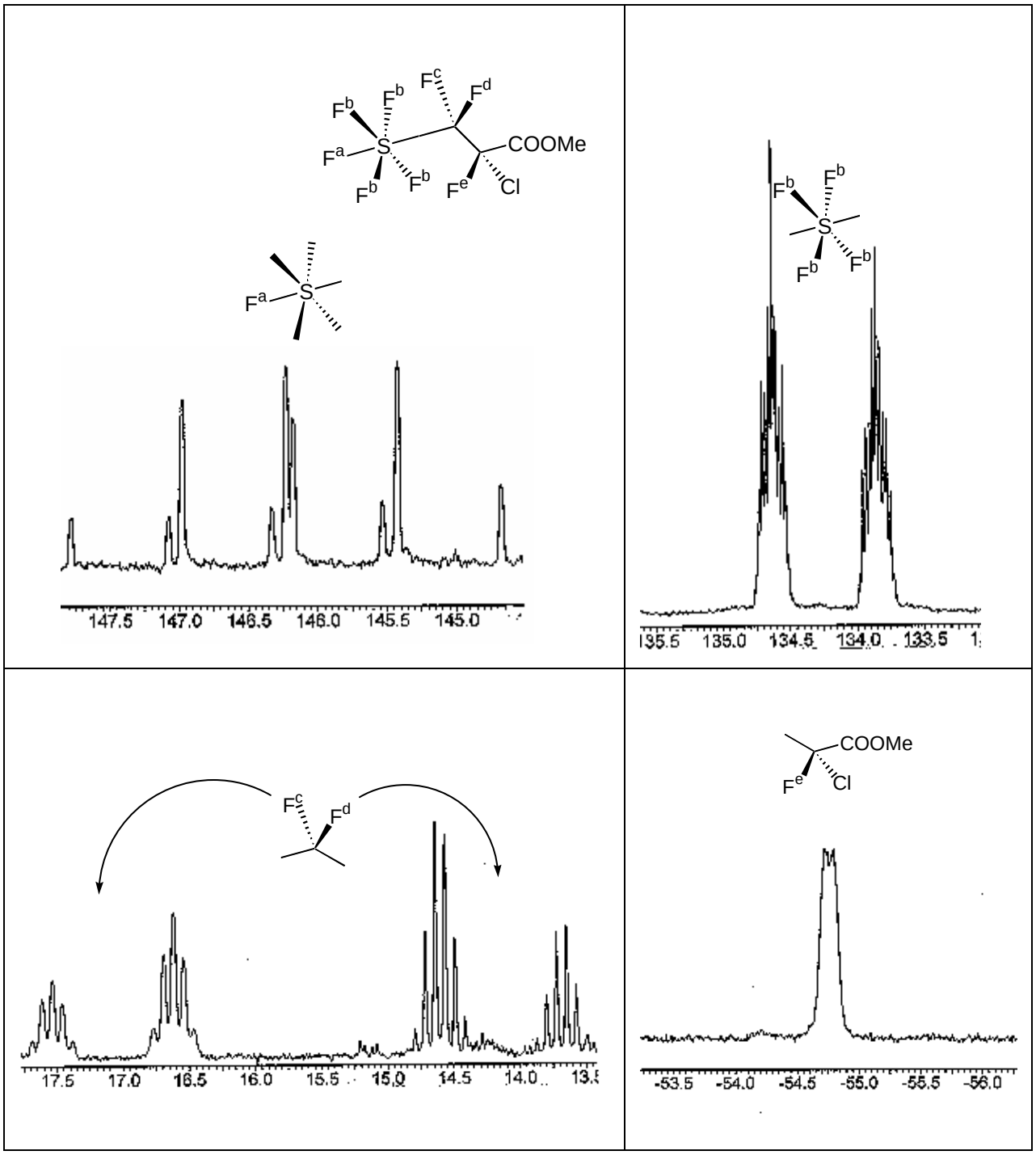
So, we tried to develop the alternative approach to the synthesis of pentafluorosulfanyl-substituted perfluoroalkanoic acids using photoinitiated addition of F_5S radical to perfluorinated derivatives of acrylic acid. Analogous radical additions of F_5SCl and F_5SBr to non-fluorinated acrylic acid derivatives are known but related functionalization of fluorinated acrylates has not been yet reported.

As a starting compound, we have used methyl trifluoroacrylate. It was mixed in quartz reactor with two equiv of pentafluorosulfanyl chloride and irradiated by UV light (450 W lamp) at room temperature. The extent of transformation has been monitored by measurement of pressure. It was found that pressure was changed during 24 h and does not decreased after this period.



Scheme 16

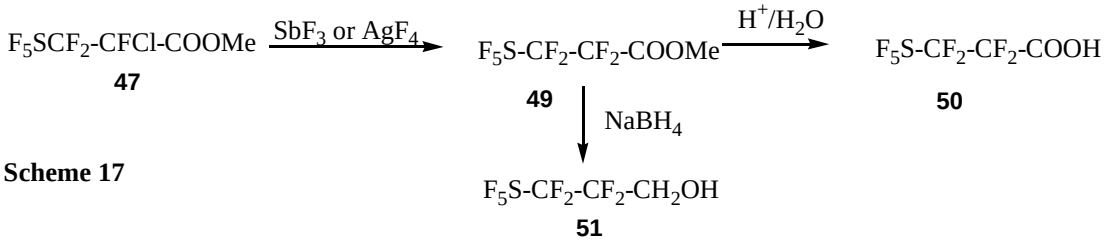
It was found that complex mixture of both low-molecular compounds and polymerization products is formed at these reaction conditions. A mixture of adducts **47** and **48** in a ratio of *ca.* 1:1.2 has been isolated by vacuum distillation. Redistillation of this mixture at ambient pressure using rectification column allows to isolate 2-chloro-2,3,3-trifluoro-3-pentafluorosulfanylpropionic acid methyl ester in a yield of 34%. Its structure has been determined by ^{19}F NMR spectroscopy data (see Figure). The spectrum consists of four groups of signals in the region from –55 to +146 ppm. The most downfield signal at +146 ppm corresponds to apical fluorine atom of pentafluorosulfanyl group with characteristic AB_4 spin system and, as a result, is splitting on nine lines.



Doublet of multiplets at 134.24 ppm ($J_{F,F}$ = 146.6 Hz) corresponds to four equatorial fluorine atoms of F_5S group. Two fluorine atoms of -CF_2- group form AB spin system (F^c, δ 17.00 ppm, F^d, δ 14.25 ppm) with vicinal coupling constant J_{F^c,F^d} = 171.0 Hz. At last, fluorine atom of

chloro(fluoro)methylene moiety has a chemical shift at –54.75 ppm. ^{1}H NMR spectrum of this compound consists of singlet at *ca*. 4 ppm confirming the presence of methoxycarbonyl fragment.

We have synthesized methyl 2,2,3,3-tetrafluoro-3-pentafluorosulfanylpropionate **49** according to described procedures using SbF_3[00] or $AgBF_4$.[00] In the case of SbF_3 the yield of **49** was 24%; the application of $AgBF_4$ allowed to increase the yield of this step to 39%. The synthesized ester has been transformed by standard methods to acid **50**[00] and alcohol **51**[00] in the yields of 72% and 65%, respectively.



Scheme 17

Structures of the obtained compounds **49** – **51** have been proved by NMR spectroscopy. The obtained NMR spectra correspond to the published data.[16] Compounds **50** and **51** have been used during the next stages of the project realization.

7. Synthesis of heterocyclic compounds containing pentafluorosulfanyl moiety

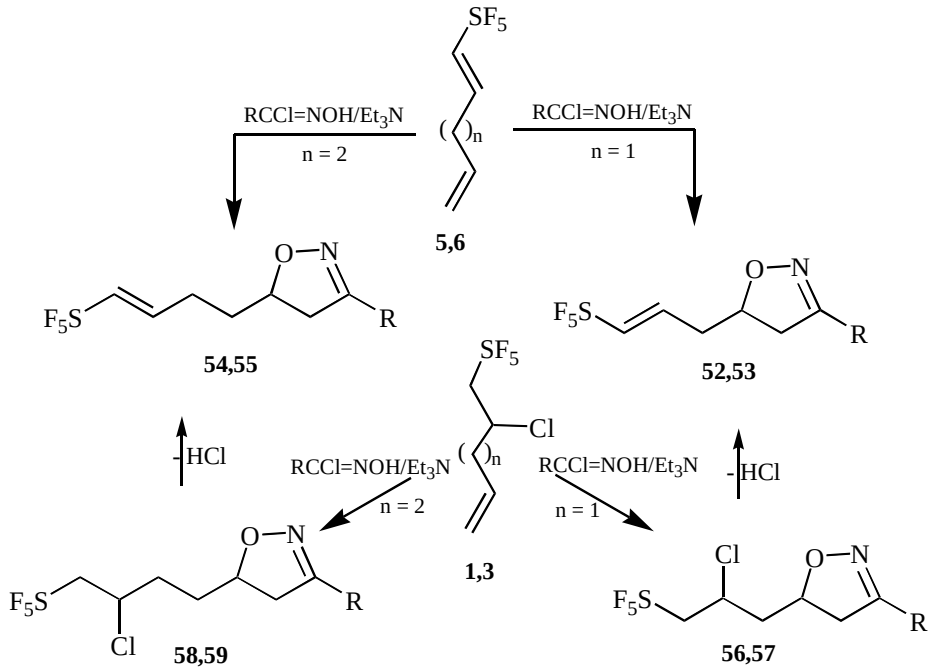
- Synthesis of dihydroisoxazoles with pentafluorosulfanyl (F_5S-) fragment.

Many biologically active compounds contain isoxazole moiety; isoxazoles show a broad spectrum of pharmacological activity.[17] Moreover, isoxazoles are useful intermediates in organic synthesis and can be used as precursors for the preparation of γ-aminoalcohols, β-hydroxyketones and other valuable products. By a present time, a large number of different isoxazoles have been synthesized and studied. However, any data on pentafluorosulfanyl-containing isoxazoles are absent hitherto. Due to our interest to the development of new organic compounds with pentafluorosulfanyl substituent and according to the research plan of this project we decided to synthesize some F_5S-containing derivatives of 4,5-dihydroisoxazoles.

Isoxazole derivatives are usually prepared by 1,3-dipolar cycloaddition reactions between different dipolarophiles and nitrile oxides.[18] Nitrile oxides can be generated by dehydration of nitro compounds or by dehydrochlorination of hydroximidoyl chlorides with different bases. We have

applied both approaches for synthesis of nitrile oxides and tried to use pentafluorosulfanyl-substituted alkenes **1, 3**, **5**, and **6** as dipolarophiles.

Firstly, we have studied 1,3-dipolar cycloaddition reactions of benzonitrile oxide and its 4-fluoro derivative with alkadienes **5** and **6** (Scheme 18). Because nitrile oxides are usually not stable these species have been prepared *in situ* in the presence of dipolarophiles. Firstly, we synthesized nitrile oxides by two-step procedure wherein the first step is the chlorination of aldoxime by *N*-chlorosuccinimide and the second step is dehydrochlorination of the resulting hydroximidoyl chloride with triethylamine. [3+2]-Cycloaddition reactions of the formed nitrile oxides to dipolarophiles **1, 3**, **5**, and **6** have been performed in diethyl ether at –20 to -15°C.

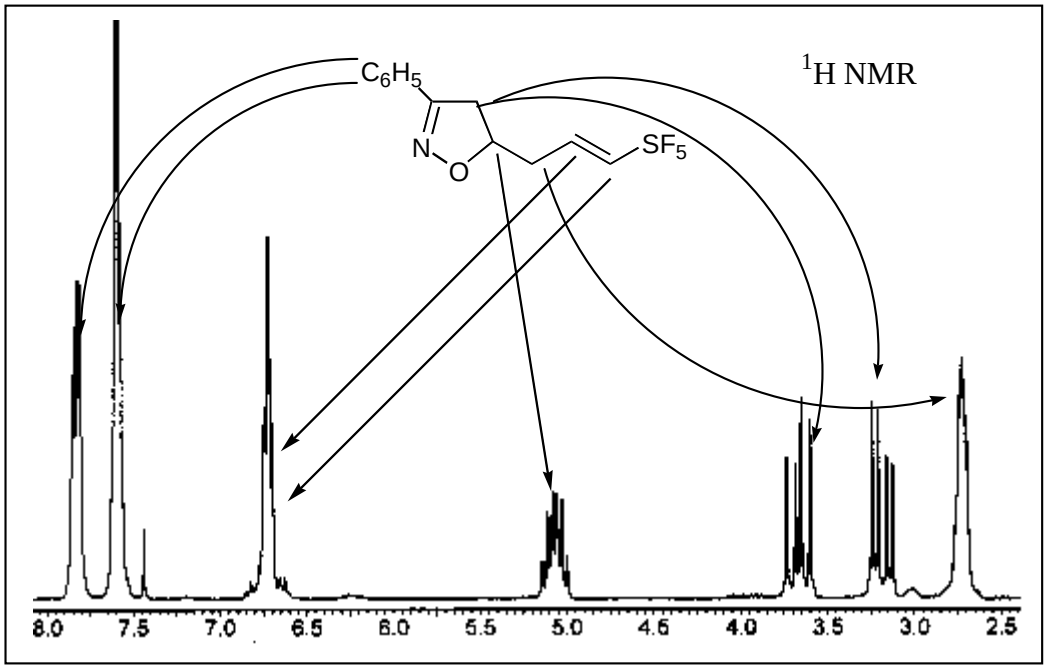


Scheme 18

In the optimized procedure, ether solution of triethylamine was added dropwise to the mixture of arylhydroximidoyl chloride and dipolarophile during 2 h. Compounds **5** and **6** react smoothly with nitrile oxides leading to 4,5-dihydroisoxazoles **52 - 55** in the yield of *ca*. 80% (Scheme 18). For alkadienes **5** and **6** it was shown that double bond connected to pentafluorosulfanyl group does not react with nitrile oxides. Oppositely, another double bond reacts smoothly with benzonitrile oxides.

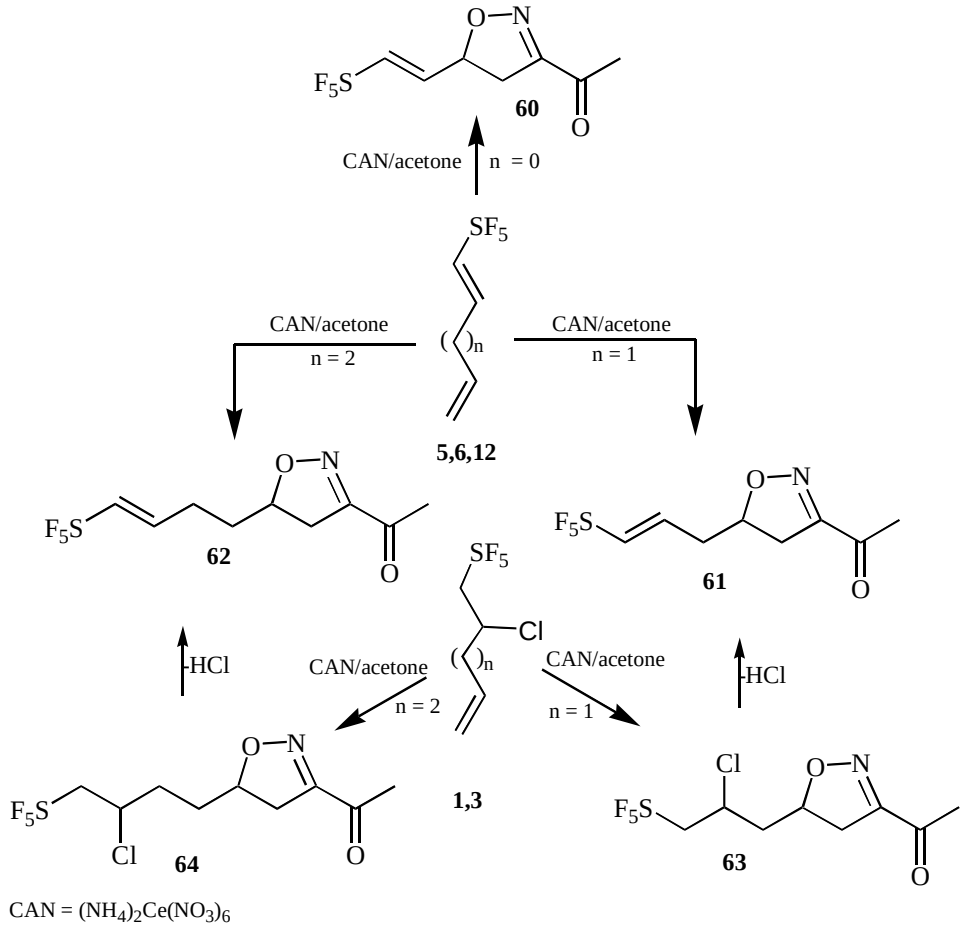
Moreover, F_5S group deactivated both double bonds of conjugated dienes: at the same reaction conditions 1-pentafluorosulfanylbuta-1,3-diene (**12**) fails to interact with benzonitrile oxides.

We have found that 4,5-dihydroisoxazoles **52 - 55** can be also obtained from alkenes **1** and **3** what are the products of F_5SCl addition to the corresponding unconjugated dienes. These 1,3-dipolar cycloadditions are simple and efficient. The formed 4,5-dihydroisoxazoles **56 - 59** have been isolated as mixtures of diastereomers in a ratio of *ca*. 1:1. Dehydrochlorinations of compounds **56 - 59** by K_2CO_3 yield products **52 - 55**. The structures of the synthesized isoxazoles **52 - 59** have been proved by ^1H, ^{13}C, and ^{19}F NMR spectroscopy data.



The generation of nitrile oxides by dehydrochlorination of hydroximidoyl chlorides is applied usually for the synthesis of different 3-aryl- and 3-alkylisoxazoles. However, this method is not efficient for the preparation of some other isoxazoles with different functional groups. Therefore, we have obtained 3-acetylisoxazoles using another procedure. These compounds have been prepared by reaction of dipolarophiles **1, 3, 5, 6,** and **12** with acetone solution of ceric ammonium nitrate $(NH_4)_2Ce(NO_3)_6$ (CAN)[19] (Scheme 19). Refluxing alkadienes **5, 6,** and **12** in acetone with CAN for 8 h yields 3-acetyl-4,5-dihydroisoxazoles **60 - 62**. Yields of these reactions are larger than 85%. The possible mechanism consists of reaction of acetone with CAN followed by *in situ* transformation of formed nitroacetone to acetonitrile oxide. The formed 1,3-dipole adds to substrates **1, 3, 5, 6,** and **12** leading to the goal isoxazolines **60 - 64**. It is needed to point out that 1-

pentafluorosulfanylbuta-1,3-diene (**12**) does not formed cycloadduct with benzonitrile oxides generated through hydroximidoyl chloride but yielded isoxazoline **60** in reaction with acetone and CAN. Alkenes **1** and **3** react with this system similarly giving 4,5-dihydroisoxazoles **63** and **64**. The structures of isoxazolines **60 - 64** have been unambiguously proved by ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy data.

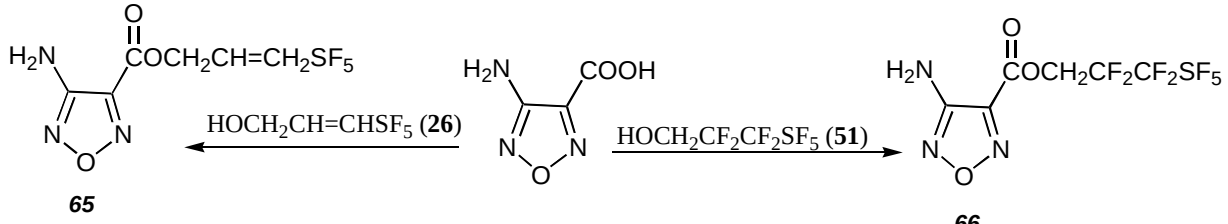


Scheme 19

- Synthesis of furazans with pentafluorosulfanyl (F_5S-) fragment

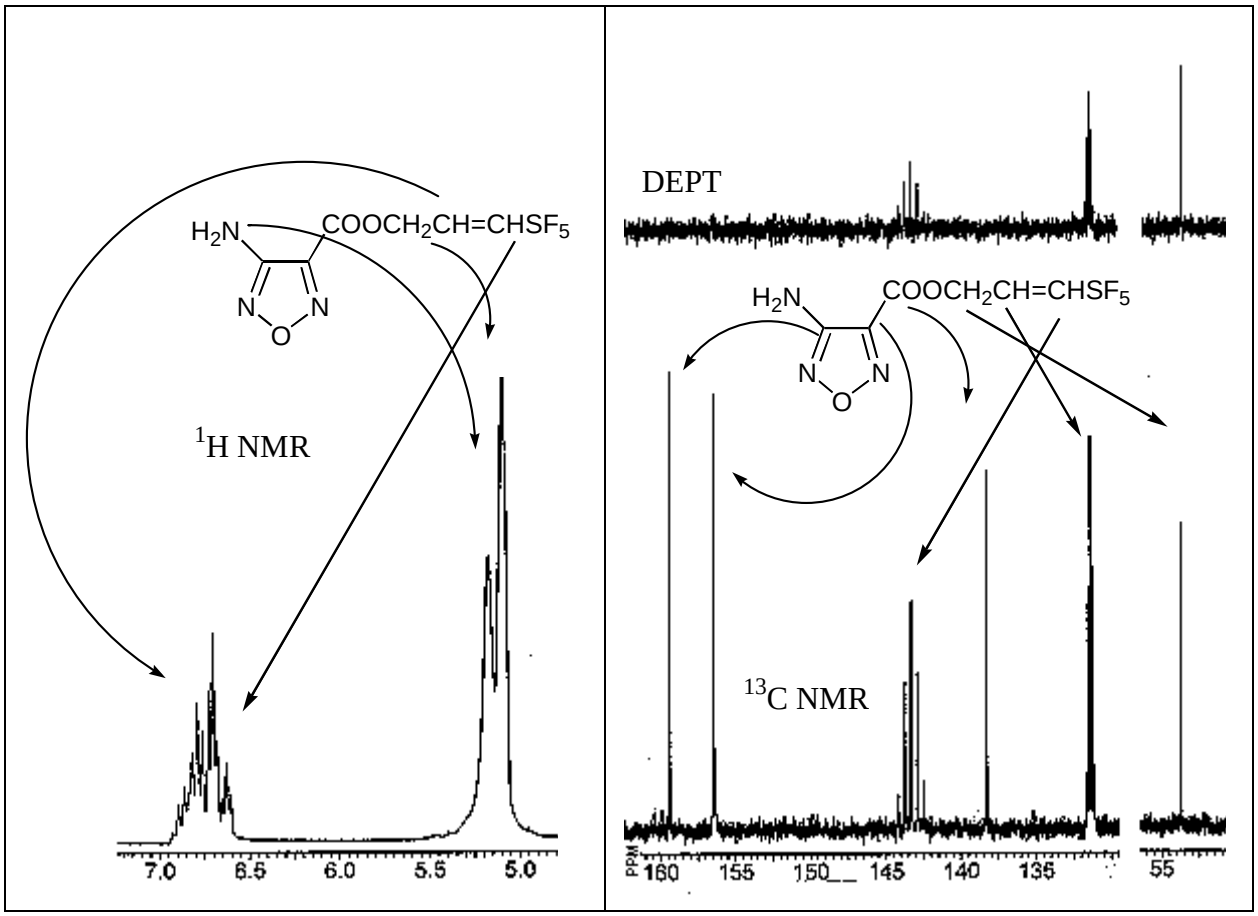
The next our goal was a synthesis of pentafluorosulfanyl-substituted 1,2,5-oxadiazole derivatives. As starting compounds to their preparation we have used furazan derivatives. For example, 4-amino-1,2,5-oxadiazole-3-carboxylic acid has been condensed with alcohols **26** and **51** in absolute 1,2-dimethoxyethane using standard procedure with dicyclohexylcarbodiimide (DCC) and 4-(dimethylamino)pyridine (DMAP) as coupling agents. Products **65** and **66** have been isolated in the

yields of 75 and 77%, respectively, by column chromatography on silica gel with chloroform/acetone (10:1) mixture as eluent.



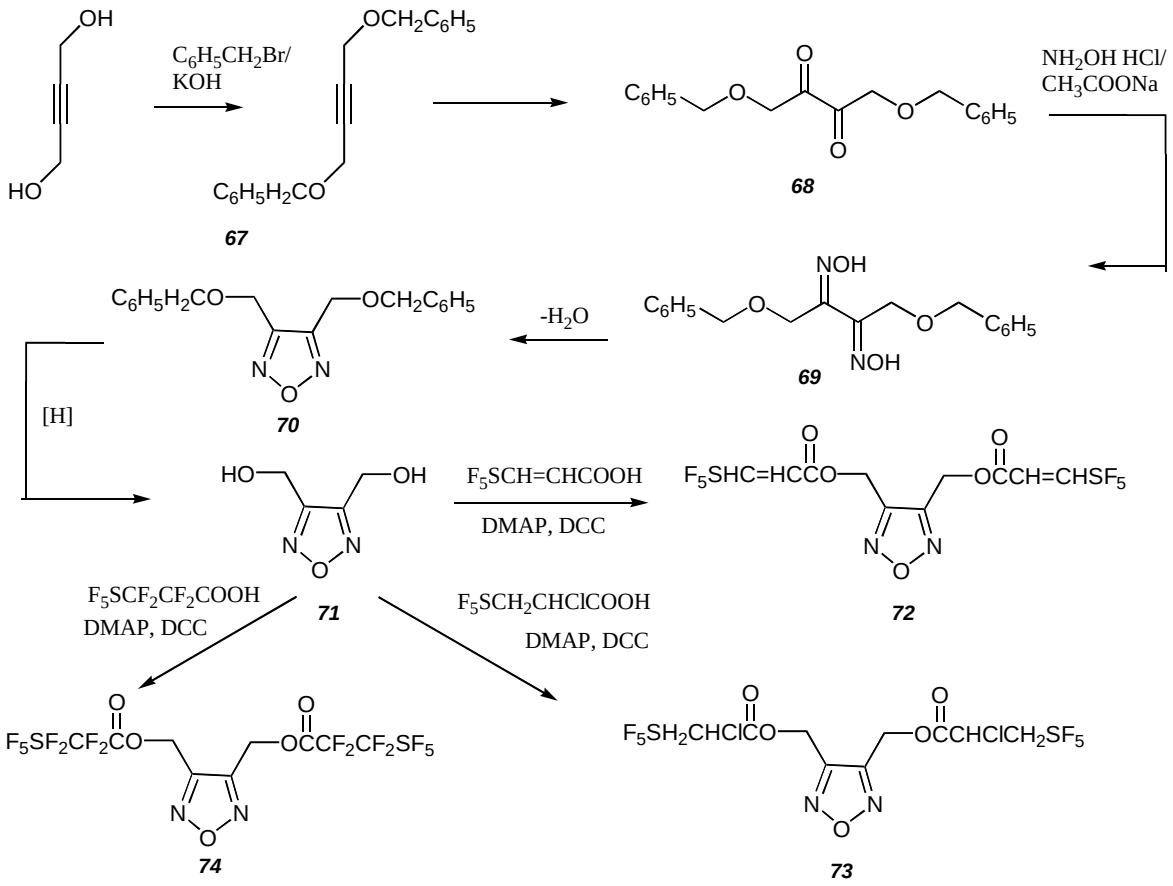
Scheme 20

The structures of the synthesized esters **65** and **66** have been unambiguously determined by analysis of ^{1}H, ^{13}C and ^{19}F NMR spectra. Thus, carbon atoms of furazan ring in compound **65** are appeared in ^{13}C NMR spectrum at 159.38 ppm and 156.46 ppm in accordance with data for other furazans.[20] Signal at 142.89 ppm can be concerned for carbon atom connected with pentafluorosulfanyl group due to its splitting to doublet of quintets. Carbonyl carbon atom has typical shift at 138.28 ppm. At last, second CH= and CH_2 groups resonate at 131.59 ppm and 53.74, respectively.



Furthermore, the ^{19}F NMR spectrum of furazan **65** consists of characteristic signals of fluorine atoms of pentafluorosulfanyl group. Apical fluorine is appeared at 159.46 ppm as nine lines because the presence of AB_4 spin system. Doublet of multiplets at 141.24 ppm ($J_{F,F}$ = 146.6 Hz) is typical signal for four equatorial fluorine atoms of F_5S group.

Synthesis of pentafluorosulfanyl-containing acids **28, 31,** and **50** has been described above. We have used these acids for acylation of 3,4-bis(hydroxymethyl)furazan. This furazan has been synthesized from 1,4-dihydroxy-2-butyne by five-step procedure (Scheme 21). The first step is protection of hydroxy groups with benzyl bromide. Dibenzyl ether **67** was oxidized by literature procedure[21] to diketone **68**. Reaction of this diketone with hydroxylamine hydrochloride[22] gave dioxime **69** what has been isolated in 64% yield by column chromatography. Dehydration[23] of the obtained dioxime gave rise to furazan **70**. At last, benzyl groups have been removed by standard deprotection procedure. The synthesized 3,4-bis(hydroxymethyl)furazan **71** has been acylated by acids **28, 31,** and **50** using standard coupling procedure with DCC and DMAP. Diesters **72 – 74** have been isolated in the yields of 32, 41, and 27%, respectively, by column chromatography.



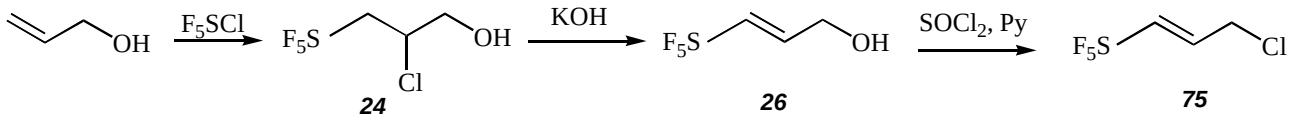
Scheme 21

The structures of the synthesized furazans have been proved by ^{1}H, ^{13}C, and ^{19}F spectroscopy data. Thus, ^{19}F NMR spectra of all three compounds **72** – **74** consist of nine lines at 146 (for **74**) or 159 (for **72** and **73**) ppm. As discussed before, it is characteristic signal of apical fluorine atom of pentafluorosulfanyl group; this kind of splitting agrees with the presence of AB_4 spin system. Another characteristic signal is doublet of multiplets at 135-144 ppm due to four equatorial fluorine atoms of SF_5 group. Moreover, two AB systems at 25 ppm and –50 ppm are seen for furazan **74** containing perfluoroalkanoate function.

8. Investigation of reactivity of allylic systems with pentafluorosulfanyl (F_5S-) fragment

Allylic systems have a broad scope in organic synthesis due to their high reactivity and ability to form different kinds of products with or without allylic rearrangement depending on their structure, the nature of reagent and reaction conditions. In the course of our investigations of the synthesis and

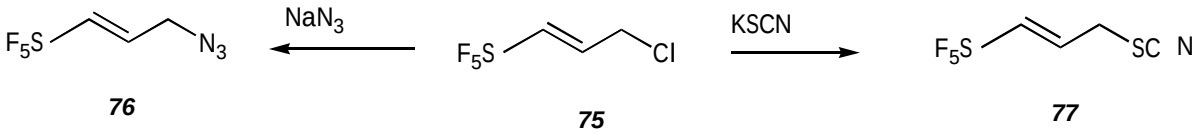
reactivity of pentafluorosulfanyl-containing organic compounds, we have synthesized 3-chloro-1-pentafluorosulfanylpropene **75** by a three-step sequence (Scheme 22).



24 ***26*** ***75***

Scheme 22

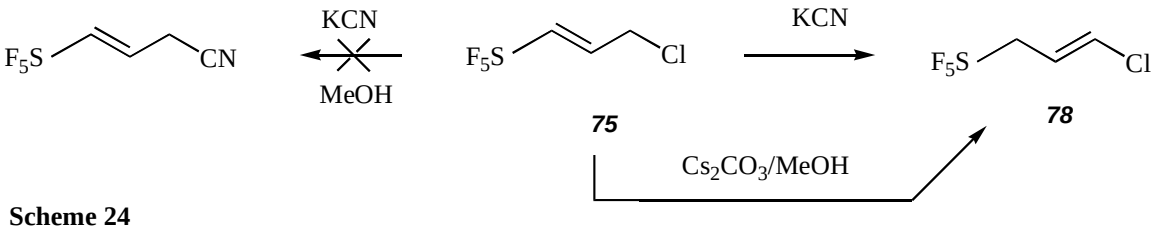
The pentafluorosulfanyl group has been introduced into allyl alcohol **2** by gas-phase radical addition of F_5SCl followed by alkali treatment, analogously to known method of pentafluorosulfanylethene preparation. Standard treatment of the resulting alcohol **26** with thionyl chloride gave the corresponding allyl chloride **75**. With the intention of preparing some heteroaromatic compounds containing pentafluorosulfanyl group (thiazoles, triazoles, tetrazoles, *etc*.), we have studied the reactions of **75** with different nucleophiles. It was found that this substrate reacts smoothly with sodium azide at 40-50°C yielding nucleophilic substitution product **76** in *ca.* 83 % yield. Similarly, treatment with potassium thiocyanate gave rise to the corresponding product **77** (Scheme 23).



76 ***75*** ***77***

Scheme 23

However, reaction of **75** with KCN failed to give the nucleophilic substitution product. Instead of allylnitrile, we have isolated 1-chloro-3-pentafluorosulfanylpropene **78** (Scheme 24).

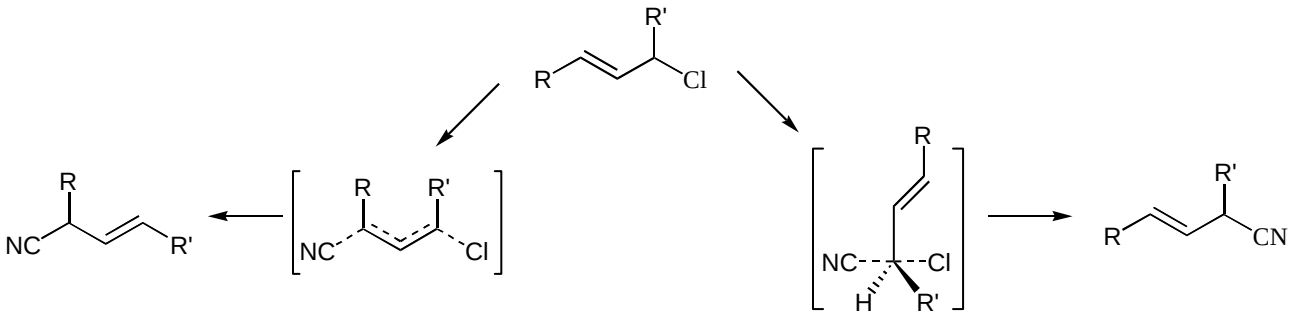


75 ***78***

Scheme 24

This result was quite unexpected since allyl chlorides are usually very good substrates for nucleophilic substitution reactions. Indeed, we have found a single literature example of similar

nucleophile-induced double bond migration in substituted allyl chlorides: treatment of 3-chloro-3-(4-nitrophenyl)propene with triethylamine gave rise to the corresponding styrene derivative. Moreover, cyanide is usually considered to be one of the best nucleophile with relatively low basicity.[24] Therefore, S_N2 or S_N2' reactions are expected in reactions of cyanide ion with allylic substrates (Scheme 25).



Scheme 25

We have calculated[8] the structure and properties of **75** to understanding the effect of the SF_5-substituent on the chemical behavior of the allyl chloride (Table 1). The obtained results showed that nucleophilic attack on an α carbon atom of **75** is a charge-controlled reaction but orbital control moves attack of nucleophile to the γ carbon. However, the bulkiness of the pentafluorosulfanyl group prevents S_N2' reaction.

Table 1. The contributions of α and γ carbon atoms of **$F_5SCH=CHCH_2Cl$ (75)** into LUMO, ξ, and charges on these atoms, *Q*, calculated at MP2/6-311G** levels.

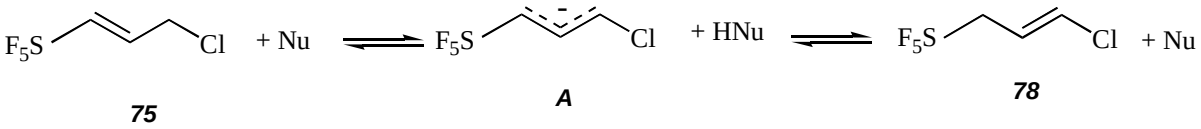
ξCα	ξCγ	*Q*Cα	*Q*Cγ	*Q*CH_2	*Q*CH
0.18	0.42	-0.20	-0.31	0.13	-0.12

As a result, even soft nucleophiles react with **75** by an S_N2 mechanism. All three studied anions (N_3^-, SCN^-, CN^-) are good nucleophiles but weak bases.[24] Cyanide is the most basic of them. Earlier we showed that the basicity of the nucleophile is an important factor in S_N2/S_N2' competition: the higher is the basicity of the nucleophile, the more preferable is an attack on the γ carbon atom. Electron-withdrawing groups in the substrate also favour the S_N2' mechanism. This is why the energy barrier for S_N2 reaction of cyanide ion with **75** is higher than that for azide or

thiocyanate ions. At the same time, steric demands of pentafluorosulfanyl group prevent S_N2' reaction. But the basicity of cyanide ion has one more effect: cyanide can deprotonate an appropriate substrate. The base-catalyzed nature of isomerization of **75** to **78** is supported by fact that treatment of **75** with slightly more basic potassium carbonate leads to the same result. Proton transfer is a fast process for exothermic reactions between O-, N- and S-atoms but is relatively slow for CH-acids. It has been explained by nonperfect synchronization between the extent of proton transfer and extent of delocalization of negative charge in the developing carbanion.[25] The more efficient is mesomeric stabilization of carbanion, the slower is proton transfer from a CH-acid with the same acidity. However, the electron-withdrawing effect exerted by the pentafluorosulfanyl group is believed to be inductive rather than mesomeric. Therefore, proton transfer from **75** must be fast for exothermic processes.

We have calculated the reaction energy for deprotonation of **75** by different anions as well as for the overall transformation of **75** into **78** (Table 2). It was found that isomerization process is moderately exothermic: calculations at the HF/6-31G, MP2/6-311G**, and MP2/6-311++G** levels gave reaction energies of -5.5, -3.8, and -4.3 kcal/mol, respectively. The data in Table 2 demonstrate that both azide and thiocyanate ions are too weak bases for deprotonation of **75** or **78**. However, in the case of cyanide ion, both deprotonation of **75** leading to allyl anion **A** and its reprotonation with the formation of **78** are exothermic processes. The low reactivity of **75** in nucleophilic substitution reactions explains the unusual behavior of cyanide but "normal" reactivity of azide and thiocyanate ions. In the case of cyanide, the exothermic proton transfer predominates. For last two ions deprotonation is highly endothermic and, therefore, is unreal process. So, a single possible process in reactions of **75** with azide and thiocyanate ions is S_N2 reaction.

Table 2. Reaction energies for processes **75** + Nu^- ⇆ **A** + HNu, and **A** + HNu ⇆ **78** + Nu^-



75 ***A*** ***78***

calculated at MP2/6-311++G** level, kcal/mol.

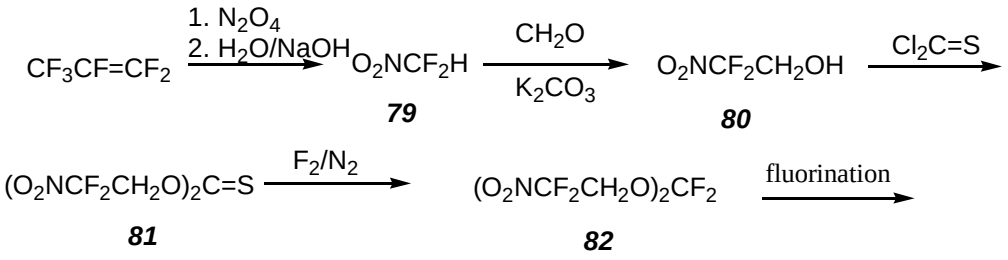
Nu	**75** + Nu ⇆ **A** + HNu	**A** + HNu ⇆ **78** + Nu
CN	-2.9	-1.4

N_3	11.0	-15.3
SCN	32.6	-36.9

It was found that N_3^- and SCN^- react with 3-chloro-1-pentafluorosulfanylprop-1-ene by S_N2 reaction but treatment of this substrate with CN^- leads to 1-chloro-3-pentafluorosulfanylprop-1-ene by base-catalyzed double bond migration. These results were interpreted using *ab initio* calculations at MP2/6-311++G** level. It was shown that proton transfer from **75** to cyanide ion is an exothermic process. It is not the case for other studied nucleophiles. At the same time, compound **75** is unreactive substrate in S_N2' processes and has low reactivity in S_N2 reactions. The structures of **75-78** were proved by ^1H, ^{19}F and ^{13}C NMR spectroscopy.

9. Exploring the fluorination of thionocarbonates and acetals

The research plan of the project includes not only the development of new approach to pentafluorosulfanyl-containing organic compounds but also the investigations of possibility to synthesize fluorinated ethers a kind of $(O_2NCF_2CF_2O)_2CF_2$. We were going to obtain this compound by reaction sequence given on Scheme 26.



Scheme 26

Using this approach, we have synthesized compound **82** by four-step procedure. At the first step we have obtained difluoronitromethane **79**. It has been further converted to 2,2-difluoro-2-nitroethanol **80** by the Henry condensation with formaldehyde. Treatment of the resulting alcohol with thiophosgene leads to thionocarbonate **81** what has been transformed into **82** by direct fluorination with 10% F_2/N_2 gas mixture. The last reaction is a key step of this synthesis.

For fluorination of ether **82** we have used different fluorine-nitrogen and fluorine-air gas

mixtures. We want to point out that related fluorination of CH_2O group was described for ethers $R_fCH_2OCFClCF_2Cl$. That reaction was performed under UV irradiation in the presence of NaF. We have applied this procedure to fluorination of **82** in quartz reactor. Process was monitored by GLC analysis of reaction samples. It was found that fluorination products did not formed at the temperature region from -25° to -15°C. Increase of reaction temperature to -5°C leads to fluorination of substrate. However, in this case the complex product mixture is formed. Analysis of reaction mixture by GC-MS method showed that the main components of this mixture are products of C-N and C-O bond cleavage. Besides destruction products, we have identified the formation of goal compound $(O_2NCF_2CF_2O)_2CF_2$ (m/z 374) in a chromatographic yield of 4%. Unfortunately, any attempts to optimize the yield of **82** and isolate this compound in a pure form failed.

10. Experimental section.

NMR spectra were recorded on a Bruker CXP - 200 spectrometer at 200 MHz (^{1}H NMR), 188.3 MHz (^{19}F NMR) and 50.3 MHz (^{13}C NMR). Chemical shifts for ^{1}H NMR and ^{13}C NMR are reported in ppm relative to TMS as internal standard. ^{19}F downfield shifts (δ) are expressed with a positive sign, relative to external CF_3COOH. Starting materials penta-1,4-diene, hexa-1,5-diene, 3-chloro-but-1-en, but-3-en-2-ol, *meta*-chloroperoxybenzoic acid are commercially available. Sulfur chloride pentafluoride was prepared from F_4S according literature procedure.[26]

4-Chloro-5-(pentafluoro-λ^6-sulfanyl)pent-1-en (**1**)

A mixture of 1,4-pentadiene (8.16 g, 0.12 mol), F_5SCl (16.2 g, 0.1 mol) and Cl_3CF (10 mL) contained in a Pyrex ampule was irradiated for 2 h with u.v. light from a Hanovia S500 lamp placed 30 cm distant. The reaction mixture was freed from Cl_3CF by distillation leaving 24 g of a brownish oil. The oil was distilled *in vacuo*, giving 18.5 g (80 %) of $F_5SCH_2CHClCH_2CH=CH_2$ (**1**), b.p. 48 ^{0}C (8 mm Hg) and 3.4 g (14.8 %) of $F_5SCH_2CHClCH_2CHClCH_2SF_5$ (**2**), b.p. 101 ^{0}C (2 mm Hg).

$F_5SCH_2CHClCH_2CH=CH_2$ (1).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.61 (m, 3 H, CH_2), 3.93 (dpent, 2 H, J_{H-F} = 8.0 Hz, J_{H-F} = 6.0 Hz, F_5SCH_2), 4.42 (pent, 1 H, J_{H-H} = 6.0 Hz, CHCl), 5.21 (dd, 1 H, J_{H-H} = 18.1 Hz, J_{H-H} = 1.4 Hz, =C<u>CH</u>H), 5.23 (dd, 1 H, J_{H-H} = 9.0 Hz, J_{H-H} = 1.4 Hz, =CCH<u>H</u>), 5.85 (ddt, 1 H, J_{H-H} = 18.1 Hz, J_{H-H} = 9.0 Hz, J_{H-H} = 6.9 Hz, -CH=).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 41.38 (s, CH_2), 54.26 (pent, J_{C-F} = 4.2 Hz, CHCl), 75.74 (dpent, J_{C-F} = 13.4 Hz, J_{C-F} = 1.0 Hz, F_5SCH_2), 120.04 (s, $=CH_2$), 131.62 (s, CH=).

^{19}F NMR (188.3 MHz, $CDCl_3$): δ = 144.01 (dm, 4F, J_{F-F} = 146.0 Hz), 160.83 (9 lines, 1F, J_{F-F} = 146.0 Hz).

Anal. Calcd for $C_5H_8ClF_5S$ (230.628): C, 26.04; H, 3.50; F, 41.19; S, 13.90.

Found: C, 26.12; H, 3.49; F, 41.36; S, 14.02.

$F_5SCH_2CHClCH_2CHClCH_2SF_5$ (2).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.29 (d, 1 H, J_{H-F} = 5.5 Hz, -C<u>H</u>H-), 2.33 (d, 1 H, J_{H-H} = 5.7 Hz, -CH<u>H</u>-), 3.91 (ddpent, 2 H, J_{H-F} = 8.0 Hz, J_{H-H} = 14.3 Hz, J_{H-H} = 7.7 Hz, $2F_5SC\underline{H}H$), 4.10 (ddpent, 2 H, J_{H-F} = 8.5 Hz, J_{H-H} = 14.3 Hz, J_{H-H} = 5.1 Hz, $2F_5SCH\underline{H}$), 4.69 (m, 2 H, 2CHCl).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 44.54 (pent, J_{C-F} = 1.2 Hz, CH_2), 52.44 (pent, J_{C-F} = 4.8 Hz, 2 CHCl), 75.75 (dpent, J_{C-F} = 14.0 Hz, J_{C-F} = 1.0 Hz, 2 F_5SCH_2).

^{19}F NMR (188 MHz, $CDCl_3$): δ = 144.40 (dm, 4F, J_{F-F} = 146.0 Hz), 161.20 (9 lines, 1F, J_{F-F} = 146.0 Hz).

Anal. Calcd for $C_5H_8Cl_2F_{10}S_2$ (393.137): C, 15.28; H, 2.05; F, 48.32; S, 16.31.

Found: C, 15.12; H, 1.97; F, 48.46; S, 16.44.

5-Chloro-6-(pentafluoro-λ^6-sulfanyl)hex-1-en (**3**)

According to the procedure for the synthesis of **1**, 1,5-hexadiene (9.8 g, 0.12 mol) was allowed to react with F_5SCl (16.2 g, 0.1 mol). Distillation at reduced pressure gave 20.7 g (84.7 % yield), b.p. 61 (7 mm Hg) of compound **3** and 3.1 g (12.7 % yield), b.p. 110 (2 mm Hg) of compound **4**.

$F_5SCH_2CHClCH_2CH_2CH=CH_2$ (3)

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.85 (m, 1 H, -C<u>H</u>H), 2.03 (m, 1 H, -CH<u>H</u>), 2.31 (m, 2 H, $-CH_2$), 3.90 (ddpent, 1 H, J_{H-H} = 6.2 Hz, J_{H-H} = 14.3 Hz, J_{H-F} = 8.0 Hz, $F_5SC\underline{H}H$), 4.03 (ddpent, 1 H, J_{H-H} = 6.2 Hz, J_{H-H} = 14.3 Hz, J_{H-F} = 8.0 Hz, $F_5SCH\underline{H}$), 4.36 (tt, 1 H, J_{H-H} = 6.2 Hz, J_{H-H} = 9.6 Hz, CHCl), 5.11 (ddd, 1 H, J_{H-H} = 17.1 Hz, J_{H-H} = 1.5 Hz, J_{H-H} = 1.5 Hz $=C\underline{CH}H$), 5.07 (dd, 1 H, J_{H-H} = 10.1 Hz, J_{H-H} = 1.5 Hz, J_{H-H} = 1.0 Hz $=CCH\underline{H}$), 5.77 (ddt, 1 H, J_{H-H} = 17.1 Hz, J_{H-H} = 10.1 Hz, J_{H-H} = 6.3 Hz, $-\underline{CH}=CH_2$).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 30.05 (s, CH_2), 36.45 (pent, J_{C-F} =14.2 Hz, CH_2), 54.92 (pent, J_{C-F} = 4.4 Hz, CHCl), 76.72 (dpent, J_{C-F} = 13.8 Hz, J_{C-F} = 0.9 Hz, F_5SCH_2), 118.57 (s, $=CH_2$), 135.82 (s, CH=).

^{19}F NMR (188.3 MHz, $CDCl_3$): δ = 144.03 (dm, 4F, J_{F-F} = 146.1 Hz), 160.96 (9 lines, 1F, J_{F-F} = 146.1 Hz).

Anal. Calcd for $C_6H_{10}ClF_5S$ (244.655): C, 29.46; H, 4.12; F, 38.83; S, 13.11.

Found: C, 29.30; H, 4.07; F, 38.97; S, 13.25.

$F_5SCH_2CHClCH_2CH_2CHClCH_2SF_5$ (4)

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.11 (m, 4 H, 2 CH_2), 3.90 (ddpent, 2 H, J_{H-F} = 8.1 Hz, J_{H-H} = 14.4 Hz, J_{H-H} = 7.1 Hz, $2F_5SC\underline{H}H$), 4.08 (ddpent, 2 H, J_{H-F} = 8.4 Hz, J_{H-H} = 14.4 Hz, J_{H-H} = 5.0 Hz, $2F_5SCH\underline{H}$), 4.42 (m, 2 H, 2CHCl).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 33.23 (pent, J_{C-F} = 1.5 Hz, CH_2), 34.19 (pent, J_{C-F} = 1.5 Hz, CH_2), 54.35 (pent, J_{C-F} = 5.5 Hz, CHCl), 54.98 (pent, J_{C-F} = 5.4 Hz, CHCl), 76.21 (dpent, J_{C-F} = 13.6 Hz, J_{C-F} = 1.0 Hz, F_5SCH_2), 76.27 (dpent, J_{C-F} = 13.4 Hz, J_{C-F} = 1.0 Hz, F_5SCH_2).

^{19}F NMR (188.3 MHz, $CDCl_3$): δ = 144.12, 144.19 (dm, 4F, J_{F-F} = 146.1 Hz). 160.47, 160.48 (9 lines, 1F, J_{F-F} = 146.1 Hz).

Anal. Calcd for $C_6H_{10}Cl_2F_{10}S_2$ (407.164): C, 17.70; H, 2.48; F, 46.66; S, 15.75.

Found: C, 17.54; H, 2.39; F, 46.80; S, 15.85.

1-(Pentafluoro-λ^6-sulfanyl)penta-1,4-dien (**5**)

To 20 g of K_2CO_3 in 50 mL sulfolane, contained in a 100 mL round-bottomed flask equipped with a magnetic stirring bar, a dropping funnel, a thermometer and a reflux condenser was added adduct **1** (6.9 g, 0.03 mol) dissolved in 10 mL of sulfolane. The mixture was stirred at r.t. for 0.5 h and at 60 ^{0}C for 3 h. When the reaction was complete, the crude product was removed under vacuum (35-40^{0}C, 1-2 mm Hg), washed with water, dried with $MgSO_4$. The crude product was isolated by column chromatography on silica gel with pentane:$CHCl_3$ (10:2) as eluent. Yield **5** (4.6 g, 79.0 %).. TLC: R_f = 0.53.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.98 (m, 2 H, CH_2), 5.13 (ddt, 1 H, J_{H-H} = 18.9 Hz, J_{H-H} = 1.4 Hz, J_{H-H} = 1.5 Hz, =C$\underline{CH}$H), 5.15 (ddt, 1 H, J_{H-H} = 10.4 Hz, J_{H-H} = 1.4 Hz, J_{H-H} = 2.1 Hz, =CCH$\underline{H}$), 5.78 (ddt, 1 H, J_{H-H} = 10.4 Hz, J_{H-H} = 18.9 Hz, J_{H-H} = 6.4 Hz, -CH=). 6.47 (m, 2 H, F_5SCH=CH).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 34.61 (s, CH_2), 118.21 (s, =CH_2), 132.60 (s, -CH=), 136.93 (pent, J_{C-F} = 7.0 Hz, F_5SCH=$\underline{CH}$), 141.30 (dpent, J_{C-F} = 19.6 Hz, J_{C-F} = 1.5 Hz, F_5SCH=).

^{19}F NMR (188.3 MHz, $CDCl_3$): δ = 140.65 (9 lines, 1F, J_{F-F} = 153.7 Hz), 161.48 (dm, 4F, J_{F-F} = 153.7 Hz).

Anal. Calcd for $C_5H_7F_5S$ (194.167): C, 30.93; H, 3.63; F, 48.92; S, 16.52.

Found: C, 30.80; H, 3.58; F, 49.10; S, 16.61.

1-(Pentafluoro-λ^6-sulfanyl)hexa-1,5-dien (**6**)

According to the procedure for the synthesis of **5**, adduct **3** (7.32 g, 0.03 mol) was allowed to react with K_2CO_3 (20 g). Distillation at reduced pressure gave 5.37 g (86 % yield) of compound **6**, b.p. 74 - 75 ^{0}C (60 mm Hg).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.23 (m, 4 H, $2CH_2$), 5.05 (dd, 1 H, J_{H-H} = 10.4 Hz, J_{H-H} = 1.4 Hz, =C<u>H</u>H), 5.07 (dd, 1 H J_{H-H} = 17.4 Hz, J_{H-H} = 1.4 Hz, =CH<u>H</u>), 5.77 (ddt, 1 H, J_{H-H} = 10.4 Hz, J_{H-H} = 17.4 Hz, J_{H-H} = 6.6 Hz, -CH=). 6.44 (m, 2 H, F_5SCH=CH).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 29.71 (s, CH_2), 31.77 (s, CH_2), 116.11 (s, =CH_2), 136.18 (s, -CH=), 138.24 (pent, J_{C-F} = 7.1 Hz, F_5SCH=<u>CH</u>), 140.71 (dpent, J_{C-F} = 19.5 Hz, J_{C-F} = 1.6 Hz, F_5SCH=).

^{19}F NMR (188.3 MHz, $CDCl_3$): δ = 140.62 (dm, 4F, J_{F-F} = 153.6 Hz), 160.91 (9 lines, 1F, J_{F-F} = 153.6 Hz).

Anal. Calcd for $C_6H_9F_5S$ (208.194): C, 34.62; H, 4.36; F, 45.63; S, 15.40.

Found: C, 34.60; H, 4.35; F, 45.76; S, 15.50.

2,3-Dichloro-1-(pentafluoro-λ^6-sulfanyl)butane (**7**)

According to the procedure for the synthesis of **1**, 3-chloro-but-1-en (9 g, 0.1 mol) was allowed to react with F_5SCl (17.8 g, 0.11 mol). Distillation at 57 ^{0}C (10 mm Hg) gave 22.9 g (91 % yield) of compound **7**.

^{1}H NMR (200 MHz, $CDCl_3$) (diastereomeric mixture): δ = 1.62, 1.70 (d, 3 H, J_{H-H} = 7.1 Hz, CH_3), 4.20 (m, 2 H, F_5SCH_2), 4.63 (m, 2 H, 2 CHCl).

^{13}C NMR (50.3 MHz, $CDCl_3$) (diastereomeric mixture): δ = 21.38, 22.19 (s, CH_3), 58.81, 59.06 (pent, J_{C-F} = 1.4 Hz, <u>CH</u>ClCH_3), 59.20, 59.59 (pent, J_{C-F} = 4.2 Hz, F_5SCH_2-<u>CHCl</u>), 74.39, 75.01 (dpent, J_{C-F} = 14.9 Hz, J_{C-F} = 1.2 Hz, F_5SCH_2).

^{19}F NMR (188.3 MHz, $CDCl_3$) (diastereomeric mixture): δ = 144.21 (dm, 4F, J_{F-F} = 146.0 Hz), 160.50 (9 lines, 1F, J_{F-F} = 146.0 Hz).

Anal. Calcd for $C_4H_7Cl_2F_5S$ (253.062): C, 18.99; H, 2.79; F, 37.54; S, 12.67.

Found: C, 18.84; H, 2.75; F, 37.68 S, 12.75.

3-Chloro-1-(pentafluoro-λ^6-sulfanyl)but-1-en (**8**)

According to the procedure for the synthesis of **5**, adduct **7** (5.06 g, 0.02 mol) was allowed to react with K_2CO_3 (11 g). Distillation at reduced pressure gave 2.17 g (50 % yield), b.p. 58 ^{0}C (80 mm Hg) of compound **8**.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.72 (d, 3 H, J_{H-H} = 7.0 Hz, CH_3), 4.59 (dq, 1 H, J_{H-H} = 8.5 Hz, J_{H-H} = 12.0 Hz, CHCl), 6.72 (m, 2 H, F_5SCH=CH).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 24.63 (s, CH_3), 53.39 (s, CHCl), 139.19 (pent, J_{C-F} = 7.1 Hz, F_5SCH=<u>CH</u>), 141.74 (dpent, J_{C-F} = 21.2 Hz, J_{C-F} = 1.7 Hz, F_5SCH=).

^{19}F NMR (188.3 MHz, $CDCl_3$): δ = 141.15 (dm, 4F, J_{F-F} = 146.9 Hz), 159.87 (9 lines, 1F, J_{F-F} = 146.9 Hz). 159.87 (9 lines, 1F, J_{F-F} = 146.9 Hz),

Anal. Calcd for $C_4H_6ClF_5S$ (216.601): C, 22.18; H, 2.79; F, 43.86; S, 14.80.

Found: C, 22.30; H, 2.83; F, 43.92; S, 14.85.

2,3-Dichlorobut-1-en (**9**)

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.75 (d, 3 H, J_{H-H} = 6.6 Hz, CH_3), 4.67 (q, 1 H, J_{H-H} = 6.6 Hz, CHCl), 5.38 (d, 1 H, J_{H-H} = 1.8 Hz, =C<u>H</u>H), 5.59 (d, 1 H, J_{H-H} = 1.8 Hz, =CH<u>H</u>).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 15.24 (s, CH_3), 47.10 (s, CHCl), 125.06 (s, $=CH_2$), 134.05 (s, =CCl).

3-Chloro-4-(pentafluoro-λ^6-sulfanyl)butane-2-ol $F_5SCH_2CHClCHOHCH_3$ (**10**)

According to the procedure for the synthesis of **1**, 3-buten-2-ol (7.2 g, 0.1 mol) was allowed to react with F_5SCl (17.82 g, 0.11 mol). Distillation at 93 ^{0}C (12 mm Hg) gave 17.8 g (76 % yield) of compound **10**.

^{1}H NMR (200 MHz, $CDCl_3$) (diastereomeric mixture): δ = 1.28 (d, 3 H, J_{H-H} = 7.4 Hz, CH_3), 1.86 (br.s, 1 H, OH), 4.00 (m, 2 H, F_5SCH_2), 4.18 (m, 1 H, CH-OH), 4.31 (m, 1 H, CHCl).

^{13}C NMR (50.3 MHz, $CDCl_3$) (diastereomeric mixture): δ = 18.80, 20.05 (s, CH_3), 60.84, 60.83 (pent, J_{C-F} = 4.0 Hz, CHCl), 68.73, 70.22 (s, CH-OH), 73.68, 74.07 (dpent, J_{C-F} = 14.2 Hz, J_{C-F} = 1.0 Hz, F_5SCH_2).

^{19}F NMR (188.3 MHz, $CDCl_3$) (diastereomeric mixture): δ = 144.16 (dm, 4F, J_{F-F} = 146.1 Hz), 144.22 (dm, 4F, J_{F-F} = 145.8 Hz), 160.82 (9 lines, 1F, J_{F-F} = 146.1 Hz), 161.00 (9 lines, 1F, J_{F-F} = 145.8 Hz).

Anal. Calcd for $C_4H_8ClF_5OS$ (234.616): C, 20.48; H, 3.44; F, 40.49; S, 13.67.

Found: C, 20.36; H, 3.37; F, 40.53; S, 13.75.

4-(Pentafluoro-λ^6-sulfanyl)but-3-en-2-ol (**11**)

To a mixture of KOH (11.2 g, 0.2 mol) in anhyd Et_2O (100 mL) in a 200 mL flask equipped with a magnetic stirring bar, thermometer and dropping funnel, was added a solution consisting of $F_5SCH_2CHClCH(OH)CH_2$ (11.7 g, 0.05 mol) in anhyd Et_2O (20 mL) dropwise at 20 – 25^{0}C. The mixture was stirred at 25 – 30^{0}C for 1.5 h, and then was added 100 ml of water. The two layers were separated and the aqueous phase was extracted with Et_2O (3 x 30 mL). The combined organic fractions were dried $MgSO_4$ and solvent was evaporated in vacuum and the resulting crude was distillation at 71 ^{0}C (12 mm Hg) gave 7.52 g (76 % yield) of compound **11**.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.39 (d, 3 H, J_{H-H} = 6.6 Hz, CH_3), 1.79 (br.s, 1 H, OH), 4.53 (m, 1 H, CH-OH), 6.53 (ddpent, 1 H, J_{H-H} = 4.4 Hz, J_{H-H} = 14.5 Hz, J_{H-F} = 1.1 Hz, =CH), 6.68 (dpent, 1 H, J_{H-H} = 14.5 Hz, J_{H-F} = 6.5 Hz, F_5SCH=).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 22.61 (s, CH_3), 65.86 (s, CH-OH), 139.86 (dpent, J_{C-F} = 20.5 Hz, J_{C-F} = 1.6 Hz, F_5SCH=), 141.39 (pent, J_{C-F} = 6.5 Hz, =CH).

^{19}F NMR (188.3 MHz, $CDCl_3$): δ = 141.16 (dm, 4F, J_{F-F} = 150.6 Hz), 161.28 (9 lines, 1F, J_{F-F} = 150.6 Hz).

Anal. Calcd for $C_4H_7F_5OS$ (198.155): C, 24.25; H, 3.56; F, 47.94; S, 16.18.

Found: C, 24.33; H, 3.59; F, 47.86; S, 16.10.

1-(Pentafluoro-λ^6-sulfanyl)but-1,3-diene (**12**)

The 4-(pentafluoro-λ^6-sulfanyl)but-3-en-2-ol (4.0 g, 0.02 mol) were treated with concd H_2SO_4 (1 mL) at –20 ^{0}C in a 10 mL flask equipped with a magnetic stirring bar, thermometer and connected with the vacuum pump (50 mm Hg) through trap cooled to – 196 ^{0}C. The mixture was stirred at 40 – 50 ^{0}C for 20 min and at 60 – 70 ^{0}C for 1 h. The liquid from trap was washed with 10% aqueus $NaHCO_3$ and water. The organic layer was dried over anhydrous sodium sulfate. Distillation at 52 ^{0}C (100 mm Hg) gave 1.44 g (40 % yield) of compound **12**.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.55 (dd, 1 H, J_{H-H} = 10.0 Hz, J_{H-H} = 0.9 Hz, =C<u>H</u>H), 5.63 (ddpent, 1 H, J_{H-H} = 16.9 Hz, J_{H-H} = 0.9 Hz, J_{H-F} = 0.9 Hz, =CH<u>H</u>), 6.29 (ddd, 1 H, J_{H-H} = 16.9 Hz, J_{H-H} = 10.0 Hz, J_{H-H} = 11.5 Hz, -<u>CH</u>=CH_2), 6.58 (dpent, 1 H, J_{H-H} = 14.5 Hz, J_{H-F} = 6.7 Hz, F_5S<u>CH</u>=CH), 6.88 (ddpent, 1 H, J_{H-H} = 14.5 Hz, J_{H-H} = 11.5 Hz, J_{H-F} = 0.8 Hz, F_5SCH=<u>CH</u>).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 126.54 (s, =CH_2), 131.35 (s, <u>CH</u>=CH_2), 136.62 (pent, J_{C-F} = 7.5 Hz, F_5SCH=<u>CH</u>), 141.74 (dpent, J_{C-F} = 20.4 Hz, J_{C-F} = 1.6 Hz, F_5SCH=).

^{19}F NMR (188.3 MHz, $CDCl_3$): δ = 141.41 (dm, 4F, J_{F-F} = 149.3 Hz), 161.53 (9 lines, 1F, J_{F-F} = 149.3 Hz).

Anal. Calcd for $C_4H_5F_5S$ (180.140): C, 26.67; H, 2.80; F, 52.73; S, 17.80.

Found: C, 26.65; H, 2.81; F, 52.76; S, 17.82.

3,4-Epoxy-1-(pentafluoro-λ^6-sulfanyl)but-1-en (**13**)

m-(Chloroperoxy)benzoic acid (3.44 g, 0.02 mol) in dichloromethane (20 mL) was added to a well-stirred solution of the compound **12** (1.8 g, 0.01 mol) in dichloromethane (20 mL) at rt. The reaction mixture was stirred for 2 h at 40 ^{0}C and 3 days at rt. Progress of the reaction was monitored by TLC. The mixture was filtered, and washed with 20% aqueous Na_2SO_3, and again with 10% aqueus NaHCO3 and water. The organic layer was dried over anhydrous sodium sulfate. Evaporation of the solvent and distillation at 80 ^{0}C (60 mm Hg) gave 1.76 g (90 % yield) of compound **13**.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.74 (dd, 1 H, J_{H-H} = 2.4 Hz, J_{H-H} = 5.4 Hz, -C<u>H</u>H), 3.12 (dd, 1 H, J_{H-H} = 5.4 Hz, J_{H-H} = 4.4 Hz, -CH<u>H</u>), 3.47 (m, 1 H, CH), 6.33 (ddpent, 1 H, J_{H-H} = 6.2 Hz, J_{H-H} = 14.6 Hz, J_{H-H} = 1.2 Hz, F_5SCH=<u>CH</u>), 6.79 (dpent, 1 H, J_{H-H} = 14.6 Hz, J_{H-F} = 6.4 Hz, F_5SCH=).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 49.18 (s, CH_2), 49.64 (pent, J_{C-F} = 1.0 Hz, CH), 136.59 (pent, J_{C-F} = 7.0 Hz, F_5SCH=<u>CH</u>), 143.13 (dpent, J_{C-F} = 21.6 Hz, J_{C-F} = 1.5 Hz, F_5SCH=).

^{19}F NMR (188 MHz, $CDCl_3$): δ = 140.73 (dm, 4F, J_{F-F} = 150.0 Hz), 160.03 (9 lines, 1F, J_{F-F} = 150.0 Hz).

Anal. Calcd for $C_4H_5F_5OS$ (196.139): C, 24.50; H, 2.57; F, 48.43; S, 16.35.

Found: C, 24.53; H, 2.56; F, 48.40; S, 16.33.

4,5-Epoxy-1-(pentafluoro-λ^6-sulfanyl)pent-1-en (**14**)

According to the procedure for the synthesis of **13**, 1-(pentafluoro-λ^6-sulfanyl)penta-1,4-dien (1.94 g, 0.01 mol) was allowed to react with *m*-(chloroperoxy)benzoic acid (3.44 g, 0.02 mol).

Distillation at 73 ^{0}C (25 mm Hg) gave 1.85 g (88 % yield) of compound **14**.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.37 (m, 1 H, -C<u>H</u>H-), 2.52 (m, 1 H, -CH<u>H</u>-), 2.56 (dd, 1 H, J_{H-H} = 2.6 Hz, J_{H-H} = 4.6 Hz, -C<u>H</u>H), 2.85 (dd, 1 H, J_{H-H} = 4.6 Hz, J_{H-H} = 4.6 Hz, -CH<u>H</u>), 3.07 (m, 1 H, CH), 6.56 (m, 2 H, F_5SCH=CH).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 32.58 (s, CH_2), 45.84 (s, CH_2), 49.15 (pent, J_{C-F} = 1.0 Hz, CH), 133.36 (pent, J_{C-F} = 7.0 Hz, F_5SCH=<u>CH</u>), 141.92 (dpent, J_{C-F} = 20.1 Hz, J_{C-F} = 1.5 Hz, F_5SCH=).

^{19}F NMR (188,3 MHz, $CDCl_3$): δ = 140.21 (dm, 4F, J_{F-F} = 150.6 Hz), 161.08 (9 lines, 1F, J_{F-F} = 150.6 Hz).

Anal. Calcd for $C_5H_7F_5OS$ (210.166): C, 28.58; H, 3.36; F, 45.20; S, 15.26.

Found: C, 28.62; H, 3.38; F, 45.17; S, 15.24.

5,6-Epoxy-1-(pentafluoro-λ^6-sulfanyl)hex-1-en (**15**)

According to the procedure for the synthesis of **13**, 1-(pentafluoro-λ^6-sulfanyl)hexa-1,5-dien (2.08 g, 0.01 mol) was allowed to react with *m*-(chloroperoxy)benzoic acid (3.44 g, 0.02 mol).

Distillation at 87 - 88 ^{0}C (8 mm Hg) gave 2.06 g (92 % yield) of compound **15**.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.77 (m, 2 H, -CH_2-), 2.39 (m, 2 H, -CH_2-), 2.54 (dd, 1 H, J_{H-H} = 2.6 Hz, J_{H-H} = 4.8 Hz, -C<u>H</u>H), 2.83 (dd, 1 H, J_{H-H} = 4.0 Hz, J_{H-H} = 4.8 Hz, -C<u>H</u>H), 2.98 (m, 1 H, CH), 6.54 (m, 2 H, F_5SCH=CH).

^{13}C NMR (50.3 MHz, MHz, $CDCl_3$): δ = 27.54 (s, CH_2), 31.19 (pent, J_{C-F} = 1.0 Hz, CH_2), 47.40 (s, CH_2), 51.50 (s, CH), 138.25 (pent, J_{C-F} = 7.0 Hz, F_5SCH=<u>CH</u>), 141.49 (dpent, J_{C-F} = 20.0 Hz, J_{C-F} = 1.5 Hz, F_5SCH=).

^{19}F NMR (188.3 MHz, $CDCl_3$): δ = 140.44 (dm, 4F, J_{F-F} = 150.6 Hz), 161.65 (9 lines, 1F, J_{F-F} = 150.6 Hz).

Anal. Calcd for $C_6H_9F_5OS$ (224.193): C, 32.15; H, 4.05; F, 42.37; S, 14.30.

Found: C, 32.31; H, 4.09; F, 42.30; S, 14.24.

2-Chloro-4,5-epoxy-1-(pentafluoro-λ^6-sulfanyl)pentane (**16**)

According to the procedure for the synthesis of **13**, adduct **1** (2.3 g, 0.01 mol) was allowed to react with *m*-(chloroperoxy)benzoic acid (3.44 g, 0.02 mol). Distillation at 78 ^{0}C (5 mm Hg) gave 2.21 g (80 % yield) of compound **16**.

^{1}H NMR (200 MHz, $CDCl_3$) (diastereomeric mixture): δ = 1.86 – 2.96 (m, 2 H, -CH_2-), 2.91 (dd, 1 H, J_{H-H} = 2.4 Hz, J_{H-H} = 4.4 Hz, -C<u>H</u>H), 2.90 (dd, 1 H, J_{H-H} = 4.4 Hz, J_{H-H} = 4.8 Hz, -C<u>H</u>H), 3.24 (m, 1 H, CH), 4.08 (dpent, 2 H, J_{H-H} = 6.4 Hz, J_{H-F} = 8.0 Hz, F_5SCH_2), 4.62 (m, 1 H, CHCl).

^{13}C NMR (50.3 MHz, $CDCl_3$) (diastereomeric mixture): δ = 40.52, 41.35 (pent, J_{C-F} = 0.8 Hz, CH_2), 46.38, 47.80 (s, CH_2), 48.81, 49.57 (s, CH), 53.46, 53.51 (pent, J_{C-F} = 4.6 Hz, CHCl), 76.90 (pent, 13.8 Hz, F_5SCH_2).

^{19}F NMR (1883 MHz, $CDCl_3$) (diastereomeric mixture): δ = 143.89 (dm, 4F, J_{F-F} = 143.1 Hz), 144.27 (dm, 4F, J_{F-F} = 146.9 Hz), 160.54 (9 lines, 1F, J_{F-F} = 143.1 Hz), 160.74 (9 lines, 1F, J_{F-F} = 146.9 Hz).

Anal. Calcd for $C_5H_8ClF_5OS$ (246.627): C, 24.35; H, 3.27; F, 38.52; S, 13.00.

Found: C, 24.42; H, 3.29; F, 38.43 S, 13.08.

2-Chloro-5,6-epoxy-1-(pentafluoro-λ^6-sulfanyl)hexane (**17**)

According to the procedure for the synthesis of **13**, adduct **3** (2.44 g, 0.01 mol) was allowed to react with *m*-(chloroperoxy)benzoic acid (3.44 g, 0.02 mol). Distillation at 80 ^{0}C (2 mm Hg) gave 2.08 g (80 % yield) of compound **17**.

^{1}H NMR (200 MHz, $CDCl_3$) (diastereomeric mixture): δ = 1.52 – 2.29 (m, 4 H, 2 -CH_2-), 2.54 (dd, 1 H, J_{H-H} = 2.5 Hz, J_{H-H} = 4.6 Hz, -C<u>H</u>H), 2.83 (dd, 1 H, J_{H-H} = 4.2 Hz, J_{H-H} = 4.6 Hz, -C<u>H</u>H), 2.96 (m, 1 H, CH), 4.00 (dpent, 2 H, J_{H-H} = 6.2 Hz, J_{H-F} = 8.0 Hz, F_5SCH_2), 4.50 (m, 1 H, CHCl).

^{13}C NMR (50.3 MHz, $CDCl_3$) (diastereomeric mixture): δ = 29.16, 29.70 (s, CH_2), 34.06, 34.69 (pent, J_{C-F} = 1.4 Hz, CH_2), 47.18, 47.33 (s, CH_2), 51.29, 51.80 (s, CH), 55.58, 55.86 (pent, J_{C-F} = 4.5 Hz, CHCl), 73.10 (dpent, J_{C-F} = 0.8 Hz, J_{C-F} = 13.4 Hz, F_5SCH_2).

^{19}F NMR (188.3 MHz, $CDCl_3$) (diastereomeric mixture): δ = 144.1 (dm, 4F, J_{F-F} = 145.0 Hz), 160.8 (9 lines, 1F, J_{F-F} = 145.0 Hz),

Anal. Calcd for $C_6H_9ClF_5OS$ (259.646): C, 27.76; H, 3.49; F, 36.58; S, 12.35.

Found: 27.84; H, 3.53; F, 36.50; S, 12.31.

2-(Pentafluoro-λ^6-sulfanyl)-1-ethyl hydroperoxyd (18).

Solution of NaOH (3.5 mL H_2O, 0.8 g NaOH) was added to a vigorously stirred solution of $F_5SCH{=}CH_2$ (6.16 g, 0.04 mole), 30% H_2O_2 (11.5 mL, 0.12 mol) and CH3OH 40 mL at 15-20^{0}C. Stirring was continued for an additional 3 h. The mixture was diluted with cold H_2O (100 mL) and

the product extracted with ether (5 x 10 mL). The combined extracrt was washed with saturated sodium chloride. After drying over anhydrous $MgSO_4$ and removal of the ether, the residue was chromatographed on silica gel. Yield 1.5 g (60 %) of **18**.

^{1} H NMR (200 MHz, $CDCl_3$): δ = 10.12 (br s, 1 H, OOH), 4.41 (t, 2H, J_{H-H} = 6.0 Hz, CH_2O), 4.04 (m, 2H, CH_2SF_5).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 71.52 (pent, J_{C-F} = 5.0 Hz, CH_2O), 68.09 (d pent, J_{C-F} = 0.5 Hz, J_{C-F} = 12.0 Hz, CH_2SF_5).

^{19}F NMR (188 MHz, $CDCl_3$): δ = 161.87 (9 lines, $J_{F,F}$ = 146.6 Hz, 1 F), 144.32 (d m, $J_{F,F}$ = 146.6 Hz, 4 F).

3-(Pentafluoro-λ^6-sulfanyl)prop-2-enoic acid (**28**)

3-(Pentafluoro-λ^6-sulfanyl)prop-3-en-1-ol (**5**) (2.3 g, 0.0125 mol) was added dropwise to a vigorously stirred solution of chromium trioxide (5 g, 0.05 mol), glacial acetic acid (45 mL) and H_2O (5 mL). The temperature of the mixture was maintained at 7-9 ^{0}C during the addition. Stirring was continued for an additional 2 h, and the mixture was then allowed to stand at room temperature for 4 h. The mixture was diluted with H_2O (100 mL) and the product extracted with ether (5 x 40 mL). The combined extracrt was washed with saturated sodium chloride. After drying over anhydrous $MgSO_4$ and removal of the ether, the residue was fractionated, yielding 1.5 g (60 %) of **7**; bp 67-69 ^{0}C/2 mm Hg.

^{1}NMR (200 MHz, $CDCl_3$): δ = 9.85 (br s, 1 H, OH), 7.56 (d pent, 1 H, J_{H-H} = 14.8 Hz, J_{H-F} = 6.6 Hz, =$CHSF_5$), 6.63 (d pent, 1 H, J_{H-H} = 14.8 Hz, J_{H-F} = 1.2 Hz, =C*H*COOH.

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 169.08 (s, C=O), 154.50 (d pent, J_{C-F} = 0.5 Hz, J_{C-F} = 23.4 Hz, =$CHSF_5$), 126.93 (pent, J_{C-F} = 7.5 Hz, =*C*HCOOH).

^{19}F NMR (188 MHz, $CDCl_3$): δ = 156.26 (9 lines, $J_{F,F}$ = 158.3 Hz, 1 F), 140.65 (d m, $J_{F,F}$ = 158.3 Hz, 4 F).

Anal. Calcd for $C_3H_3F_5O_2S$: C, 18.19; H, 1.53; S 16.19. Found: C, 18.56; H, 1.60; S 16.02.

3-(Pentafluoro-λ^6-sulfanyl)prop-2-en-1-al (**29**)

A mixture of 3-pentafluorosulfanylprop-2-en-1-ol **(**1.68 g, 0.01 mol) and ammonium cerium (IV) nitrate (8.37 g, 0.015 mol) in 50% solution of acetic acid (25 mL) was stirred at 85-90^{0}C 0.5 h. After the orange cerium(IV) solution had turned to a pale yellow cerium(III) solution containing

a small amount of cerium (IV), the ptoduct mixture was extracted with ether. The ether solution was washed with 5% potassium hydroxide and dried. Removal of the ether by distillation left 1.5 g (90%) pure aldehyde **29.**

^{1} H NMR (200 MHz, $CDCl_3$): δ = 9.70 (d, 1 H, J_{H-H} = 6.8 Hz, CH=O), 7.36 (d pent, 1 H, J_{H-H} = 15.0 Hz, J_{H-H} = 6.2 Hz, =$CHSF_5$), 6.74 (dd, 1 H, J_{H-H} = 6.8 Hz, J_{H-H} = 15.0 Hz, =CH).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 189.72 (s, C=O), 157.63 (d pent, J_{C-F} = 1.5 Hz, J_{C-F} = 22.0 Hz, =$CHSF_5$), 134.28 (pent, J_{C-F} = 6.0 Hz, =*C*HC=O).

^{19}F NMR (188 MHz, $CDCl_3$): δ = 155.68 (9 lines, $J_{F,F}$ = 146.6 Hz, 1 F), 140.39 (d m, $J_{F,F}$ = 146.6 Hz, 4 F).

4-(Pentafluoro-λ^{6}-sulfanyl)but-3-en-2-on (**30**)

Solution of $K_2Cr_2O_7$ (1.97 g, 0.0067 mol), H_2SO_4 (1.5 mL) and H_2O (10mL) was added to a vigorously stirred solution of **6** (3.96 g, 0.02 mole) and Et_2O (50 mL) at room temperature. Stirring was continued for an additional 2 h. The two layers were separated and the aqueous phase was extracted with Et_2O (3 x 30 mL). The combined extract was washed with saturated NaCl and dried over anhydrous Na_2SO_4. After removal of the ether, the residue was fractionated, yielding 2.2 g (56%) of **8**; bp 50-56 ^{0}C/18 mm Hg).

^{1} H NMR (200 MHz, $CDCl_3$): δ = 7.28 (d pent, 1 H, J_{H-H} = 14.9 Hz, J_{H-F} = 6.6 Hz, =$CHSF_5$), 6.79 (d, 1 H, J_{H-H} = 14.9 Hz, CHC=O), 2.43 (s, 3 H, CH_3).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 195.39 (s, C=O), 151.05 (d pent, J_{C-F} = 1.5 Hz, J_{C-F} = 20.6 Hz, =$CHSF_5$), 133.18 (pent, J_{C-F} = 6.5 Hz, =*C*HC=O), 29.35 (s, CH_3).

^{19}F NMR (188 MHz, $CDCl_3$): δ = 157.23 (9 lines, $J_{F,F}$ = 150.9 Hz, 1 F), 141.00 (d m, $J_{F,F}$ = 150.9 Hz, 4 F).

Anal. Calcd for $C_4H_5F_5OS$: C, 24.49; H, 2.57; S 16.35. Found: C, 24.88; H, 1.64; S 16.36.

3-Pentafluorosulfanyl-2-chloro1propionic acid (31)

According to the procedure for the synthesis of **28**.

^{1}NMR (200 MHz, $CDCl_3$): δ = 10.63 (br s, 1 H, OH), 4.82 (dd, 1H, J_{H-H} = 9.6 Hz, J_{H-H} = 3.8 Hz, CHCl), 4.51 (dd pent, 1 H, J_{H-H} = 9.6 Hz, J_{H-H} = 16.8 Hz, J_{H-F} = 7.4 Hz, C*H*HSF_5), 4.01 (dd pent, 1 H, J_{H-H} = 3.8 Hz, J_{H-H} = 16.8 Hz, J_{H-F} = 7.4 Hz, C*H*HSF_5).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 172.31 (s, C=O), 71.76 (pent, J_{C-F} = 18.6 Hz, CH_2SF_5), 50.08 (pent, J_{C-F} = 6.0 Hz, HCCl).

^{19}F NMR (188 MHz, $CDCl_3$): δ = 156.54 (9 lines, $J_{F,F}$ = 145.7 Hz, 1 F), 144.31 (d m, $J_{F,F}$ = 145.7 Hz, 4 F).

Anal. Calcd for $C_3H_4ClF_5O_2S$: C, 15.36; H, 1.72. Found: C, 15.24; H, 1.74.

4-Pentafluorosulfanyl-3-chloroprobutyric acid (32)

According to the procedure for the synthesis of **28**.

^{1}NMR (200 MHz, $CDCl_3$): δ = 10.33 (br s, 1 H, OH), 4.41 (m, 1H, CHCl), 4.22 –4.08 (m, 2 H, CH_2SF_5), 3.62 (d pent, 2H, J_{H-H} = 6.8 Hz, CH_2COOH).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 168.75 (s, C=O), 69.45 (pent, J_{C-F} = 18.0 Hz, CH_2SF_5), 34.22 (pent, J_{C-F} = 6.0 Hz, HCCl), 22.43 (s, CH_2).

^{19}F NMR (188 MHz, $CDCl_3$): δ = 155.65 (9 lines, $J_{F,F}$ = 145.0 Hz, 1 F), 145.71 (d m, $J_{F,F}$ = 145.0 Hz, 4 F).

Anal. Calcd for $C_4H_6ClF_5O_2S$: C, 19.32; H, 2.43. Found: C, 19.48; H, 2.46.

***endo*-2-(Pentafluoro-λ^6-sulfanyl)-5-norbornene-*exo*-3-carboxylic acid (33a) and *exo*-2-(pentafluoro-λ^6-sulfanyl)-5-norbornene-*endo*-3-carboxylic acid (33b)**

A mixture of **7** (1.98 g, 0.01 mol), pentadiene (6.6 g, 0.1 mol) contained in a Pyrex seal tube was heated at 110 ^{0}C for 10 h. The reaction mixture was freed from pentadiene by evaporation under reduced pressure leaving 2.4 g of a brownish oil. Isomers **33a** and **33b** were isolated by column chromatography on silica gel.

33a; 1.34 g, (50.8%) as a colorless oil. R_f = 0.6 ($CHCl_3$/MeOH = 10:1).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 10.91 (br s, 1 H, OH), 6.48 (d d, 1 H, J_{H-H} = 5.6 Hz, J_{H-H} = 3.2 Hz, =CH), 6.30 (d d, 1 H, J_{H-H} = 5.6 Hz, J_{H-H} = 2.2 Hz, =CH), 5.00 (m, 1 H, $CHSF_5$), 3.55 (br s, 1 H, CH), 3.25 (br s, 1 H, CH), 3.02 (d d, 1 H, J_{H-H} = 5.0 Hz, J_{H-H} = 1.6 Hz, C*H*COOH), 1.67 (m, 2 H, CH_2).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 179.07 (s, C=O), 137.58 (s, =CH), 136.01 (s, =CH), 87.79 (pent, J_{C-F} = 10.0 Hz, $CHSF_5$), 49.58 (pent, J_{C-F} = 3.0 Hz, C*H*COOH), 48.33 (s, CH), 47.92 (pent, J_{C-F} = 2.5 Hz, CH), 46.06 (pent, J_{C-F} = 3.0 Hz, CH_2).

^{19}F NMR (188 MHz, $CDCl_3$): δ = 164.49 (9 lines, $J_{F,F}$ = 145.9 Hz, 1 F), 140.30 (d m, $J_{F,F}$ = 145.9 Hz, 4 F).

Anal. Calcd for $C_8H_9F_5O_2S$: C, 36.37; H, 3.43; S 12.14. Found: C, 36.50; H, 3.30; S 12.42.

33b; 0.45 g, (17%) as a colorless oil. R_f = 0.71 ($CHCl_3$/MeOH = 10:1).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 11.41 (br s, 1 H, OH), 6.29 (m, 2 H, 2CH=), 4.20 (m, 1 H, $CHSF_5$), 3.76 (d d, 1 H, J_{H-H} = 4.1 Hz, J_{H-H} = 4.0 Hz, C*H*COOH), 3.63 (m, 1 H, CH), 3.44 (m, 1 H, CH), 1.95 (d, 1 H, J_{H-H} = 9.2 Hz, C*H*H), 1.80 (d, 1 H, J_{H-H} = 9.0 Hz, CH*H*).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 178.03 (s, C=O), 137.82 (s, =CH), 136.45 (s, =CH), 88.29 (pent, J_{C-F} = 9.0 Hz, $CHSF_5$), 48.97 (pent, J_{C-F} = 3.5 Hz, *C*HCOOH), 48.72 (pent, J_{C-F} = 4.0 Hz, CH), 48.43 (pent, J_{C-F} = 1.0 Hz, CH_2), 46.37 (s, CH).

^{19}F NMR (188 MHz, $CDCl_3$): δ = 165.27 (9 lines, $J_{F,F}$ = 142.0 Hz, 1 F), 139.43 (d m, $J_{F,F}$ = 142.0 Hz, 4 F).

Anal. Calcd for $C_8H_9F_5O_2S$: C, 36.37; H, 3.43; S 12.14. Found: C, 36.48; H, 3.30; S 12.45.

***endo*-2-(Pentafluoro-λ^6-sulfanyl)-5-norbornene-*exo*-3-carboxylic acid (34a) and *exo*-2-(pentafluoro-λ^6-sulfanyl)-5-norbornene-*endo*-3-carboxylic acid (34b)**

According to the procedure for the synthesis of **33**.

34a; 1.43 g, (56.3%) as a colorless oil. R_f = 0.56 ($CHCl_3$).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 9.641 (d, 1 H, J_{H-H} = 5.6 Hz, CH=O), 6.47 (d d, 1 H, J_{H-H} = 5.6 Hz, J_{H-H} = 3.0 Hz, =CH), 6.29 (d d, 1 H, J_{H-H} = 5.6 Hz, J_{H-H} = 2.2 Hz, =CH), 4.76 (m, 1 H, $CHSF_5$), 3.30 (br s, 1 H, CH), 3.15 (br s, 1 H, CH), 2.22 (d d, 1 H, J_{H-H} = 5.0 Hz, J_{H-H} = 1.6 Hz, CHCO), 1.67 (m, 2 H, CH_2).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 167.07 (s, C=O), 137.23 (s, =CH), 135.92 (s, =CH), 84.80 (pent, J_{C-F} = 10.0 Hz, $CHSF_5$), 47.08 (pent, J_{C-F} = 3.0 Hz, CHCO), 48.33 (s, CH), 47.73 (pent, J_{C-F} = 2.5 Hz, CH), 46.04 (pent, J_{C-F} = 2.5 Hz, CH_2).

^{19}F NMR (188 MHz, $CDCl_3$): δ = 163.41 (9 lines, $J_{F,F}$ = 145.0 Hz, 1 F), 140.21 (d m, $J_{F,F}$ = 145.0 Hz, 4 F).

Anal. Calcd for $C_8H_9F_5OS$: C, 38.71; H, 3.66; S 12.92. Found: C, 38.59; H, 3.61; S 12.80.

34b; 0.45 g, (17%) as a colorless oil. R_f = 0.71 ($CHCl_3$/MeOH = 10:1).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 9.60 (br s, 1 H, OH), 6.23 (m, 2 H, 2CH=), 4.02 (m, 1 H, $CHSF_5$), 3.45 (m, 1 H, C*H*CH=O), 3.60 (m, 1 H, CH), 3.42 (m, 1 H, CH), 1.96 (d, 1 H, J_{H-H} = 9.0 Hz, C*H*H), 1.80 (d, 1 H, J_{H-H} = 9.0 Hz, CH*H*).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 176.003 (s, C=O), 137.74 (s, =CH), 136.40 (s, =CH), 88.12 (pent, J_{C-F} = 9.0 Hz, $CHSF_5$), 44.32 (pent, J_{C-F} = 3.5 Hz, *C*HCH=O), 48.52 (pent, J_{C-F} = 4.0 Hz, CH), 48.89 (pent, J_{C-F} = 1.0 Hz, CH_2), 46.32 (s, CH).

^{19}F NMR (188 MHz, $CDCl_3$): δ = 165.12 (9 lines, $J_{F,F}$ = 142.0 Hz, 1 F), 140.21 (d m, $J_{F,F}$ = 142.0 Hz, 4 F).

Anal. Calcd for $C_8H_9F_5OS$: C, 38.71; H, 3.66; S 12.92. Found: C, 38.61; H, 3.59; S 12.96.

exo-3-Acetyl-_endo_-2-(pentafluoro-λ^6-sulfanyl)-5-norbornene (35a) and _endo_-3-acetyl-_exo_-2-(pentafluoro-λ^6-sulfanyl)-5-norbornene (35b)

A mixture of **30** (1.96 g, 0.01 mol), pentadiene (6.6 g, 0.1 mol) contained in a Pyrex seal tube was heated at 60 ^{0}C for 10 h. The reaction mixture was freed from pentadiede by evaporation under reduced pressure leaving 2.32 g of a brownish oil. Isomers **35a** and **35b** were isolated by column chromatography on silica gel.

35a; 0.95 g, (36.3%) as a colorless oil. R_f = 0.56 ($CHCl_3$/hexane = 10:2).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 6.45 (d d, 1H, J_{H-H} = 5.4 Hz, J_{H-H} = 3.2 Hz, =CH), 6.25 (m, 1 H, =CH), 5.09 (m, 1 H, $CHSF_5$), 3.48 (br s, 1 H, CH), 3.13 (br s, 1 H, CH), 3.02 (d, 1 H, J_{H-H} = 4.8 Hz, C*H*$COCH_3$), 2.33 (s, 3 H, CH_3), 1.51 (br s, 2 H, CH_2).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 205.93 (s, C=O), 137.23 (s, =CH), 136.42 (s, =CH), 86.44 (pent, J_{C-F} = 9.0 Hz, $CHSF_5$), 56.89 (pent, J_{C-F} = 3.0 Hz, *C*H$COCH_3$), 47.63 (pent, J_{C-F} = 2.5 Hz, CH), 46.99 (s, CH), 45.22 (pent, J_{C-F} = 3.0 Hz, CH_2), 29.93 (s, CH_3).

^{19}F NMR (188 MHz, $CDCl_3$): δ = 165.38 (9 lines, $J_{F,F}$ = 145.0 Hz, 1 F), 140.41 (d m, $J_{F,F}$ = 145.0 Hz, 4 F).

Anal. Calcd for $C_9H_{11}F_5OS$: C, 41.22; H, 4.23; S 12.23. Found: C, 41.32; H, 4.29; S 12.40.

35b; 0.32 g, (12.2%) as a colorless oil. R_f = 0.67 ($CHCl_3$/hexane = 10:2).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 6.24 (d d, 1 H, J_{H-H} = 5.6 Hz, J_{H-H} = 3.6 Hz, =CH), 6.05 (d d, 1H, J_{H-H} = 5.6 Hz, J_{H-H} = 2.6 Hz, =CH), 4.34 (m, 1 H, $CHSF_5$), 3.80 (d d, 1 H, J_{H-H} = 4.0 Hz, J_{H-H} = 4.0 Hz, C*H*$COCH_3$), 3.59 (d pent, 1 H, J_{H-H} = 4.0 Hz, J_{H-F} = 4.0 Hz, CH), 3.39 (br s, 1 H,

CH), 2.26 (s, 3 H, CH_3), 1.97 (d, 1 H, J_{H-H} = 8.8 Hz, C*H*H), 1.82 (d d, 1 H, J_{H-H} = 8.8 Hz, J_{H-H} = 1.2 Hz, CH*H*).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 204.30 (s, C=O), 136.36 (pent, J_{C-F} = 1.0 Hz, =CH), 136.30 (s, =CH), 86.60 (d pent, J_{C-F} = 0.5 Hz, J_{C-F} = 8.7 Hz, $CHSF_5$), 56.66 (pent, J_{C-F} = 3.3 Hz, $CHCOCH_3$), 48.67 (pent, J_{C-F} = 1.5 Hz, CH), 48.56 (s, CH_2), 46.18 (s, CH), 29.08 (s, CH_3).

^{19}F NMR (188 MHz, $CDCl_3$): δ = 165.46 (9 lines, $J_{F,F}$ = 143.5 Hz, 1 F), 139.76 (d m, $J_{F,F}$ = 143.5 Hz, 4 F).

Anal. Calcd for $C_9H_{11}F_5OS$: C, 41.22; H, 4.23; S 12.23. Found: C, 41.40; H, 4.31; S 12.38.

1,2-Dimethyl-4-(pentafluoro-λ^6-sulfanyl)cyclohex-1-en-5-carboxylic acid (36)

According to the procedure for the synthesis of **33.**

^{1}H NMR (200 MHz, $CDCl_3$): δ = 11.20 (br s, 1 H, OH), 4.61 (oct, 1 H, J_{H-H} = 6.6 Hz, $CHSF_5$), 3.32 (d t, 1 H, J_{H-H} = 7.1 Hz, J_{H-H} = 6.6 Hz, *C*HCOOH), 2.68 (m, 2 H, CH_2), 2.51 (m, 2 H, CH_2), 1.69 (s, 3 H, CH_3), 1.68 (s, 3 H, CH_3).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 179.91 (pent, J_{C-F} = 1.0 Hz, C=O), 123.35 (s, =C), 122.86 (pent, J_{C-F} = 1.0 Hz, =C), 83.39 (d pent, J_{C-F} = 1.5 Hz, J_{C-F} = 9.2 Hz, $CHSF_5$), 43.56 (pent, J_{C-F} = 2.0 Hz, *C*HCOOH), 34.11 (pent, J_{C-F} = 1.3 Hz, CH_2), 33.43 (pent, J_{C-F} = 4.6 Hz, CH_2), 19.60 (s, CH_3), 19.08 (s, CH_3).

^{19}F NMR (188 MHz, $CDCl_3$): δ = 163.03 (9 lines, $J_{F,F}$ = 141.8 Hz, 1 F), 134.20 (d m, $J_{F,F}$ = 141.8 Hz, 4 F).

Anal. Calcd for $C_9H_{13}F_5OS$: C, 38.57; H, 4.68; S 11.44. Found: C, 38.23; H, 4.62; S 11.21.

1-Methyl-4-(pentafluoro-λ^6-sulfanyl)cyclohex-1-en-5-carboxylic acid and 1-methyl-5-(pentafluoro-λ^6-sulfanyl)cyclohex-1-en-4-carboxylic acid (37)

According to the procedure for the synthesis of **33.**

^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.47, 5.39 (m, H, =CH), 4.62 (oct, 1 H, J_{H-H} = 6.6 Hz, $CHSF_5$), 3.40, 3.32 (d t, 1 H, J_{H-H} = 6.6 Hz, J_{H-H} = 6.0 Hz, *CH*COOH), 2.77 – 2.49 (m, 4 H, $2CH_2$), 1.74 (s, 3 H, CH_3).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 179.58, 179.47 (pent, J_{C-F} = 1.0 Hz, C=O), 131.66, 130.85 (s, =C), 118.15, 117.55 (s, =C), 82.81, 82.23 (d pent, J_{C-F} = 1.5 Hz, J_{C-F} = 9.2 Hz, $CHSF_5$), 43.00,

42.08 (pent, $J_{C\text{-}F}$ = 2.5 Hz, *C*HCOOH), 32.02, 27.63 (pent, $J_{C\text{-}F}$ = 1.3 Hz, CH_2), 31.68, 27.57 (pent, $J_{C\text{-}F}$ = 4.6 Hz, CH_2), 23.40, 23.10 (s, CH_3).

^{19}F NMR (188 MHz, $CDCl_3$): δ = 163.14, 163.10 (9 lines, 1 F), 134.25, 133.84 (d m, $J_{F,F}$ = 141.0 Hz, 4 F).

Anal. Calcd for $C_8H_{11}F_5OS$: C, 38.40; H, 4.43; S 12.81. Found: C, 38.53; H, 4.46 S 12.96.

5-Acetyl-1,2-dimethyl-4-(pentafluoro-λ^6-sulfanyl)cyclohex-1-en (38)

According to the procedure for the synthesis of **33.**

^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.62 (oct, 1 H, $J_{H\text{-}H}$ = 6.8 Hz, $CHSF_5$), 3.36 (d t, 1 H, $J_{H\text{-}H}$ = 6.8 Hz, $J_{H\text{-}H}$ = 7.4 Hz, C*H*COOH), 2.71 (d d, 1H, $J_{H\text{-}H}$ = 8.3 Hz, $J_{H\text{-}H}$ = 18.0 Hz, C*H*H), 2.62 (d d, 1 H, $J_{H\text{-}H}$ = 5.5 Hz, $J_{H\text{-}H}$ = 18.0 Hz, CH*H*), 2.42 (d d, 1 H, $J_{H\text{-}H}$ = 5.6 Hz, $J_{H\text{-}H}$ = 17.5 Hz, C*H*H), 2.28 (s, 3 H, CH_3), 2.23 (d d, 1 H, $J_{H\text{-}H}$ = 6.3 Hz, $J_{H\text{-}H}$ = 17.5 Hz, C*H*H), 1.69 (s, 3 H, CH_3), 1.68 (s, 3 H, CH_3).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 207.83 (s, C=O), 123.47 (pent, $J_{C\text{-}F}$ = 1.0 Hz, =CH), 123.22 (br s, =CH), 83.95 (d pent, $J_{C\text{-}F}$ = 0.9 Hz, $J_{C\text{-}F}$ = 9.0 Hz, $CHSF_5$), 50.20 (pent, $J_{C\text{-}F}$ = 2.5 Hz, C*H*C=O), 34.43 (pent, $J_{C\text{-}F}$ = 1.3 Hz, CH_2), 33.94 (pent, $J_{C\text{-}F}$ = 5.1 Hz, CH_2), 28.93 (pent, $J_{C\text{-}F}$ = 1.0 Hz C(O)*CH*$_3$), 19.04 (s, CH_3), 18.63 (s, CH_3).

^{19}F NMR (188 MHz, $CDCl_3$): δ = 164.59 (9 lines, $J_{F,F}$ = 141.4 Hz, 1 F), 135.05 (d m, $J_{F,F}$ = 141.4 Hz, 4 F).

Anal. Calcd for $C_{10}H_{15}F_5O_2S$: C, 43.16; H, 5.43; S 11.52. Found: C, 43.50; H, 5.38; S 11.81.

3-Chloro-4-(pentafluoro-λ^6-sulfanyl)butan-1-ol (41)

A mixture of but-1-en-4-ol (7.2 g, 0.1 mol), F_5SCl (17.82 g, 0.11 mol) and Cl_3CF (10 mL) contained in a Pyrex seal tube was irradiated at room temperature for 2 h with UV light from a Hanovia S500 lamp placed at a distance of 15-20 cm. The reaction mixture was freed from Cl_3CF by distillation leaving 22 g of a brownish oil. The oil was distilled in vacuo, giving 20.5 g (87 %) of **41**; bp 90-93 ^{0}C/5 mm Hg.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.58 (m, 1 H, CHCl), 4.00 (m 2 H, CH_2SF_5), 3.85 (m, 2 H, CH_2OH), 2.19 (m, 1 H, C*H*H), 1.86 (m, 1 H, CH*H*), 2.06 (s, 1 H, OH).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 76.92 (d pent, $J_{C,F}$ = 13.4 Hz, $J_{C,F}$ = 1.0 Hz, CH_2SF_5), 58.73 (s, CH_2OH), 52.76 (pent, $J_{C,F}$ = 4.5 Hz, CHCl), 39.55 (pent, $J_{C,F}$ = 1.3 Hz, CH_2).

^{19}F NMR (188 MHz, $CDCl_3$): δ = 161.18 (9 lines, $J_{F,F}$ = 148.3 Hz, 1 F). 144.30 (d m, $J_{F,F}$ = 148.3 Hz 4 F),

Anal. Calcd for $C_4H_8ClF_5OS$: C, 20.48; H, 3.44; S 13.67. Found: C, 20.56; H, 3.50; S 13.59.

4-(Pentafluoro-λ^6-sulfanyl)but-3-en-1-ol (**42**)

To a solution of **41** (11.73 g, 0.05 mol) in anhyd Et_2O (100 mL) in a 200 mL flask equipped with a magnetic stirring bar, thermometer and powder addition funnel, was added a powder of KOH (11.2 g, 0.2 mol) at 20 – 25^{0}C. The mixture was stirred at 25 – 30^{0}C for 1.5 h, and then was added to H_2O (150 mL). The two layers were separated and the aqueous phase was extracted with Et_2O (3 x 30 mL). The combined organic fractions were dried ($MgSO_4$) and the solvent was evaporated in vacuum and the resulting crude was distilled to give 7.52 g (76 % yield) of compound **42**; bp 64-65 ^{0}C/2 mm Hg.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 6.50 (m, 2 H, HC=CH), 3.73 (t, 2 H, CH_2OH), 2.41 (m. 2 H, CH_2), 2.23 (s, 1 H, OH).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 142.02 (d pent, $J_{C,F}$ = 19.5 Hz, $J_{C,F}$ = 1.6 Hz, =$CHSF_5$), 135.64 (pent, $J_{C,F}$ = 7.2 Hz, *CH*=$CHSF_5$), 60.37 (pent, $J_{C,F}$ = 1.0 Hz, CH_2), 33.38 (s, CH_2).

^{19}F NMR (188 MHz, $CDCl_3$): δ = 161.84 (9 lines, 1 F, $J_{F,F}$ = 149.2 Hz), 140.48 (d m, 4 F, $J_{F,F}$ = 149.2 Hz).

Anal. Calcd for $C_4H_7F_5OS$: C, 24.25; H, 3.56; S 16.18. Found: C, 24.31; H, 3.49; S 16.25.

4-(Pentafluoro-λ^6-sulfanyl)but-3-en-1-oic acid (43)

According to the procedure for the synthesis of **28**, **42** (2.48 g, 0.0125 mol) was allowed to react with CrO_3 (5 g, 0.05). Distillation at 104-106 ^{0}C/1 mm Hg gave 1.43 g, (54%) of compound **43**.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 11.82 (s, 1 H, COOH), 6.65 (m, 2 H, HC=CH), 3.32 (t, 1 H, $J_{H,H}$ = 2.0 Hz, C*H*HCOOH), 3.30 (t, 1 H, $J_{H,H}$ = 2.0 Hz, CH*H*COOH).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 176.27 (s, C=O), 143.88 (d pent, $J_{C,F}$ = 21.4 Hz, $J_{C,F}$ = 1.4 Hz, =$CHSF_5$), 130.58 (pent, $J_{C,F}$ = 7.5 Hz, *CH*=$CHSF_5$), 35.40 (s, CH_2).

^{19}F NMR (188 MHz, $CDCl_3$): δ = 159.94 (9 lines, $J_{F,F}$ = 147.6 Hz, 1 F), 140.08 (d m, $J_{F,F}$ = 147.6 Hz, 4 F).

Anal. Calcd for $C_4H_5F_5O_2S$: C, 22.65; H, 2.38; S 15.12. Found: C, 22.70; H, 2.40; S 15.19.

Methyl 4-(pentafluoro-λ^6-sulfanyl)but-3-enate (44)

Solution of **16** (2.12 g, 0.01 mol), MeOH (10 mL), benzene (40 mL) and H_2SO_4 (2 mL) was heated for 6 h. To reaction mixture was added H_2O (50 mL). The two layers were separated and the aqueous phase was extracted with Et_2O (3 x 30 mL). The combined organic fractions were dried ($MgSO_4$) and the solvent was evaporated in vacuum and the resulting crude was distilled to give 1.47 g (65 % yield) of compound **44**; bp 87-88 ^{0}C/14 mm Hg.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 6.63 (m, 2 H, HC=CH), 3.82 (s, 3 H, OCH_3), 3.26 (t, 1 H, $J_{H,H}$ = 1.8 Hz, C*H*HCOOH), 3.24 (t, 1 H, $J_{H,H}$ = 1.8 Hz, CH*H*COOH).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 169.80 (s, C=O), 143.45 (d pent, $J_{C,F}$ = 20.6 Hz, $J_{C,F}$ = 1.5 Hz, =$CHSF_5$), 131.45 (pent, $J_{C,F}$ = 7.5 Hz, *CH*=$CHSF_5$), 52.81 (s, 3 H, CH_3), 35.58 (s, CH_2).

^{19}F NMR (188 MHz, $CDCl_3$): δ = 160.64 (9 lines, $J_{F,F}$ = 149.6 Hz, 1 F), 140.50 (d m, $J_{F,F}$ = 149.6 Hz, 4 F).

Anal. Calcd for $C_5H_7F_5O_2S$: C, 26.55; H, 3.12; S 14.18. Found: C, 26.49; H, 3.20; S 14.11.

Methyl 4-(pentafluoro-λ^6-sulfanyl)but-2-enate (45)

To a solution of **17** (1.13 g, 0.005 mol) in MeOH (10 mL) was added a powder of Cs_2CO_3 (0.326 g, 0.001 mol) at room temperature and the mixture was stirred for 48 h. The solvent was removed under diminished pressure, the residual oil treated with H_2O (5 mL) and then extracted with Et_2O (3 x 30 mL). The combined extract was dried over anhydrous Na_2SO_4. After removal of the Et_2O, the residue was fractionated, yielding 0.86 g (76%) of **45**; bp 88-90 ^{0}C/14 mm Hg.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.04 (d t, 1 H, $J_{H,H}$ = 15.6 Hz, $J_{H,H}$ = 8.0 Hz, CH_2CH=), 6.12 (d, 1H, $J_{H,H}$ = 15.6 Hz, =*CH*COOH), 4.42 (d pent, 2 H, $J_{H,F}$ = 7.6 Hz, $J_{H,H}$ = 8.0 Hz, CH_2SF_5), 3.82 (s, 3 H, OCH_3).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 165.66 (s, C=O), 135.41 (pent, $J_{C,F}$ = 4.5 Hz, =*CH*CH_2SF_5), 128.71 (pent, $J_{C,F}$ = 1.0 Hz, *CH*=$CHCH_2SF_5$), 71.78 (d pent, $J_{C,F}$ = 16.6 Hz, $J_{C,F}$ = 1.0 Hz, CH_2SF_5), 52.46 (s, CH_3).

^{19}F NMR (188 MHz, $CDCl_3$): δ = 158.68 (9 lines, $J_{F,F}$ = 144.8 Hz, 1 F), 144.05 (d m, $J_{F,F}$ = 144.8 Hz, 4 F).

Anal. Calcd for $C_5H_7F_5O_2S$: C, 26.55; H, 3.12; S 14.18. Found: C, 26.50; H, 3.14; S 14.19.

Methyl 1,2-dimethyl-4-(pentafluoro-λ^6-sulfanylmethyl)-cyclohex-1-en-5-carboxylate (46)

A mixture of **45** (1.13 g, 0.005 mol), 2,3-dimethylbutadiene (3.5 g, 0.05 mol) contained in a Pyrex seal tube was heated at 100 ^{0}C for 8 h. The reaction mixture was freed from 2,3-dimethylbutadiene by evaporation under reduced pressure leaving 00 g of a brownish oil. The oil was chromatographed ($CHCl_3$/MeOH = 10:1.0) to give **46** (1.0 g, 68%) as a colorless oil. R_f = 0.88 ($CHCl_3$/hexane = 10:2).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.92-3.39 (m, 2 H, CH_2SF_5), 3.75 (s, 3 H, OCH_3), 2.74 (m, 1 H, *CH*CH_2SF_5), 2.52 (m, 1 H, *CH*COOH), 2.44-1.84 (m, 4 H, 2 CH_2), 1.64 (s, CH_3), 1.63 (s, CH_3).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 175.05 (s, C=O), 123.98 (s, =CH), 123.58 (s, =CH), 76.47 (pent, $J_{C,F}$ = 11.6 Hz, CH_2SF_5), 52.40 (s, OCH_3), 44.16 (s, CH), 36.32 (s, CH_2), 33.92 (pent, $J_{C,F}$ = 3.0 Hz, CH), 33.66 (s, CH_2), 19.28 (s, CH_3), 18.92 (s, CH_3).

^{19}F NMR (188 MHz, $CDCl_3$): δ = 163.76 (9 lines, $J_{F,F}$ = 145.0 Hz, 1 F), 145.03 (d m, $J_{F,F}$ = 145.0 Hz, 4 F).

Anal. Calcd for $C_{11}H_{17}F_5O_2S$: C, 42.85; H, 5.56; S 10.40. Found: C, 42.90; H, 5.58; S 10.43.

Methyl ether 3-(pentafluoro-λ^6-sulfanyl)-2-chloro-3,3,2-trifluoropropionic acid (47).

To a 400 mL quartz vessel 2.0 g (0.014 mol) of F_2C=CFCOOMe and 2.5 g (0.015 mol) of F_5SCl were added via a vacuum transfer. This mixture was irradiated (450W sunlamp) for 24 h at room temperature. The reaction mixture was distilled at 69-70^{0}C (80 mm Hg) giving 1.2 g (30 %) **49.**

^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.03 (s, 3H, CH_3).

^{19}F NMR (188 MHz, $CDCl_3$): δ = 146.2 (9 lines, $J_{F,F}$ = 145.0 Hz, 1 F), 134.24 (d m, $J_{F,F}$ = 146.6 Hz, 4 F), 17.00 (dd pent, $J_{F,F}$ = 171.0 Hz, $J_{F,F}$ = 16.0 Hz, $J_{F,F}$ = 10.0 Hz, 1F, CF*F*), 17.00 (dd pent, $J_{F,F}$ = 171.0 Hz, $J_{F,F}$ = 15.1 Hz, $J_{F,F}$ = 9.0 Hz, 1F, CF*F*), -64.75 (m, 1F, CClF).

Anal. Calcd for $C_4H_3ClF_8O_2S$ (302.543): C, 15.89; H, 0.99; S 10.60. Found: C, 15.66; H, 1.10; S 10.40.

Methyl ether 3-(pentafluoro-λ^6-sulfanyl)-3,3,2,2-tetrafluoropropionic acid (49).

According to the procedure for the synthesis of $F_5SCF_2CF_2Ph$.[00] To a 100 mL quartz vessel 2.0 g (0.012 mol) of $AgBF_4$, 2.67 g (0.01 mol) of **49** in 20 mL CH_2Cl_2 was added with stirring. The reaction mixture , after stirring for 3 h in room temperature, was suction filtrated and the filter cake washed of CH_2Cl_2. After removal of the CH_2Cl_2., the residue was fractionated, yielding 0.86

g (30%) of **49**; bp 110-1120 ^{0}C. The product residue was found to be identical in all aspects with an authentic sample of methyl ether 3-Pentafluorosulfanyl-3,3,2,2-tetrafluoropropionic acid.[00]

3-(Pentafluoro-λ^6-sulfanyl)-3,3,2,2-tetrafluoropropan-1-ol (50).

Sodium borohydride (0.32 g) was added to 25 g tetraglyme with rapid stirring. At room temperature 2.5 g of **(49)** was added to the sodium borohydride solution over a period of 1.5 h. The crude reaction mixture was heated to 50^{0}C and held at that temperature for 1 h. The reaction mixture then was cooled to room temperature and 50 mL water with 1 mL H_2SO_4 was added. The reaction mixture was heated to 100^{0}C, at which point an azeotrope of the **50** and water distilled from reaction mixture. The water and were phase-separated. A total of 1.2 g (45%) **(50)** was collected.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.09 (ddd, 2H, $J_{H,H}$ = 17.0 Hz, $J_{H,F}$ = 7.0 Hz, 1H, $J_{F,F}$ = 4.5 Hz, C*H*HOH), 3.98 (ddd, $J_{H,H}$ = 17.0 Hz, $J_{H,F}$ = 5.4 Hz, 1H, $J_{F,F}$ = 7.1 Hz, CH*H*OH).

^{19}F NMR (188 MHz, $CDCl_3$): δ = 144.0 (9 lines, 1F, $J_{F,F}$ = 146.0 Hz, 1 F), 133.43 (d m, 4F, $J_{F,F}$ = 146.0 Hz, 4 F), -14.00 (m, 2F, $J_{F,F}$ = 9.5 Hz, $J_{F,F}$ = 17.0 Hz, CF_2), -30.21 (m, 2F, $J_{F,F}$ = 17.0 Hz).

Anal. Calcd for $C_3H_3F_9OS$ (201.234): C, 17.89; H, 1.49; S 15.90. Found: C, 17.76; H, 1.52; S 15.76.

3-(Pentafluoro-λ^6-sulfanyl)-3,3,2,2-tetrafluoropropionic acid (51).

According to the procedure for the synthesis of **28** from **50**.

^{19}F NMR (188 MHz, $CDCl_3$): δ = 145.0 (9 lines, 1F, $J_{F,F}$ = 142.0 Hz, 1 F), 134.43 (d m, 4F $J_{F,F}$ = 142.0 Hz, 4 F), -17.00 (m, 2F, $J_{F,F}$ = 10.7 Hz, $J_{F,F}$ = 16.8 Hz, CF_2), -39.42 (m, 2F, $J_{F,F}$ = 16.8 Hz).

Anal. Calcd for $C_3HF_9O_2S$ (272.0): C, 13.24; S 11.76. Found: C, 13.49; S 11.63.

3-Phenyl-5-(1-pentafluoro-λ^6-sulfanylprop-1-en-3-yl)- 4,5-dihydroisoxazole (52).

1-Pentafluorosulfanylpenta-1,4-diene **5 (**0.194 g, 0.001 mol) is dissolved in 10 mL of ether. Phenylhydroximoyl chloride[00] (0.39 g, 0.0025 mol) in 10 mL of ether is added at –30^{0}C. Triethylamine (0.005 mol) in 5 mL ether, is added dropwise over a period of 1h. Stirring is continued at –30^{0}C until the reaction is complete according to TLC (1-2 h). The reaction is then quenched by adding 10 mL of saturated ammonium chloride. Ether extraction, drying with

$MgSO_4$, and evaporation of the solvent yield a brownish oil. Flash chromatography with chloroform gives **52** (0.23 g, 78%).

H NMR (200 MHz, $CDCl_3$): δ = 7.83 (m, 2H, Ar), 7.59 (m, 3H, Ar), 6.73 (m, 2H, CH=CH), 5.02 (m, 1H, OCH), 3.65 (dd, 1H, $J_{H,H}$ = 10.2 Hz, $J_{H,H}$ = 16.6 Hz, C*H*H), 3.16 (dd, 1H, $J_{H,H}$ = 6.8 Hz, $J_{H,H}$ = 16.6 Hz, CH*H*), 2.73 (m, 2H, CH_2CH=).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 156.80 (s, C=N), 143.40 (d pent, $J_{C,F}$ = 20.1 Hz, $J_{C,F}$ = 1.5 Hz, F_5SCH=), 134.08 (pent, $J_{C,F}$ = 7.0 Hz, *C*H=CHSF_5), 130.81 (s, CH, Ar), 129.49 (s, C, Ar), 129.23 (s, CH, Ar), 127.12 (s, CH, Ar), 79.05 (br.s, OCH), 40.09 (s, CH_2), 36.49 (s, CH_2).

^{19}F NMR (188.3 MHz, $CDCl_3$): δ = 162.61 – 159.41 (9 lines, 1F, J_{F-F} = 148.50 Hz), 140.35 (dm, 4F, J_{F-F} = 148.5 Hz).

Anal. Calcd for $C_{12}H_{12}F_5NOS$ (313.289): C, 46.01; H, 3.86; F, 30.32; N, 4.47.

Found: C, 46.24; H, 3.90; F, 30.45; N, 4.50.

3-(4-Fluorophenyl)-5-(1-pentafluoro-λ^6-sulfanylprop-1-en-3-yl)- 4,5-dihydroisoxazole (53).

According to the procedure for the synthesis of **52**.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.66 (m, 2H, Ar), 7.12 (m, 2H, Ar), 6.58 (m, 2H, CH=CH), 4.94 (m, 1H, OCH), 3.49 (dd, 1H, $J_{H,H}$ = 10.4 Hz, $J_{H,H}$ = 16.8 Hz, C*H*H), 3.04 (dd, 1H, $J_{H,H}$ = 7.0 Hz, $J_{H,H}$ = 16.8 Hz, CH*H*), 2.58 (m, 2H, CH_2CH=).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 164.28 (d, $J_{C,F}$ = 250.0 Hz, CF, Ar), 155.83 (s, C=N), 143.40 (d.pent, $J_{C,F}$ = 19.0 Hz, $J_{C,F}$ = 1.5 Hz, =CHSF_5), 134.01 (pent, $J_{C,F}$ = 7.5 Hz, *C*H=CHSF_5), 129.05 (d, $J_{C,F}$ = 8.0 Hz, CH, Ar), 125.80 (d, $J_{C,F}$ = 3.0 Hz, C, Ar), 116.34 (d, $J_{C,F}$ = 22.1 Hz, CH, Ar), 79.15 (s, OCH), 40.07 (s, CH_2), 36.40 (s, CH_2).

^{19}F NMR (188.3 MHz, $CDCl_3$): δ = 162.61 – 159.47 (9 lines, 1F, J_{F-F} = 152.0 Hz), 140.32 (dm, 4F, J_{F-F} = 152.0 Hz), -31.84 (m, 1F).

Anal. Calcd for $C_{12}H_{11}F_6NOS$ (331.279): C, 43.51; H, 3.35; F, 34.41; N, 4.23.

Found: C, 43.42; H, 3.30; F, 34.91; N, 4.11.

3-Phenyl-5-(1-pentafluoro-λ^6-sulfanylbut-1-en-4-yl)- 4,5-dihydroisoxazole (54).

According to the procedure for the synthesis of **52**.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.70 (m, 2H, Ar), 7.45 (m, 3H, Ar), 5.98 (m, 2H, CH=CH), 4.85 (m, 1H, OCH), 3.49 (dd, 1H, $J_{H,H}$ = 10.6 Hz, $J_{H,H}$ = 16.6 Hz, C*H*H), 3.05 (dd, 1H, $J_{H,H}$ = 7.6 Hz, $J_{H,H}$ = 16.6 Hz, CH*H*), 2.43 (m, 2H, C*H*$_2$CH=), 1.91 (m, 2H, C*H*$_2$CH$_2$).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 156.91 (s, C=N), 141.56 (d pent, $J_{C,F}$ = 19.6 Hz, $J_{C,F}$ = 1.0 Hz, F_5SCH=), 134.33 (pent, $J_{C,F}$ = 7.0 Hz, *C*H=CHSF$_5$), 130.60 (s, CH, Ar), 129.87 (s, C, Ar), 129.18 (s, CH, Ar), 127.03 (s, CH, Ar), 80.24 (s, OCH), 40.57 (s, CH_2), 33.99 (s, CH_2), 27.11 (s, CH_2).

^{19}F NMR (188.3 MHz, $CDCl_3$): δ = 163.51 – 160.32 (9 lines, 1F, J_{F-F} = 150.40 Hz), 140.60 (dm, 4F, J_{F-F} = 150.40 Hz).

Anal. Calcd for $C_{13}H_{14}F_5NOS$ (327.316): C, 47.70; H, 4.31; F, 29.02; N, 4.28.

Found: C, 47.58; H, 4.38; F, 29.14; N, 4.40.

3-(4-Fluorophenyl)-5-(1-pentafluoro-λ^6-sulfanylbut-1-en-4-yl)- 4,5-dihydroisoxazole (55).

According to the procedure for the synthesis of **52**.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.70 (m, 2H, Ar), 7.14 (m, 2H, Ar), 6.54 (m, 2H, CH=CH), 4.79 (m, 1H, OCH), 3.47 (dd, 1H, $J_{H,H}$ = 10.4 Hz, $J_{H,H}$ = 16.6 Hz, C*H*H), 3.02 (dd, 1H, $J_{H,H}$ = 7.6 Hz, $J_{H,H}$ = 16.6 Hz, CH*H*), 2.43 (m, 2H, C*H*$_2$CH=), 1.88 (m, 2H, C*H*$_2$CH$_2$).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 164.20 (d, $J_{C,F}$ = 250.0 Hz, CF, Ar), 155.91 (d, $J_{C,F}$ = 1.0 Hz, C=N), 141.64 (d.pent, $J_{C,F}$ = 19.6 Hz, $J_{C,F}$ = 1.5 Hz, =CHSF$_5$), 138.17 (pent, $J_{C,F}$ = 7.0 Hz, *C*H=CHSF$_5$), 128.98 (d, $J_{C,F}$ = 8.6 Hz, CH, Ar), 126.13 (d, $J_{C,F}$ = 3.5 Hz, C, Ar), 116.33 (d, $J_{C,F}$ = 22.1 Hz, CH, Ar), 80.33 (s, OCH), 40.07 (s, CH_2), 36.40 (s, CH_2).

^{19}F NMR (188.3 MHz, $CDCl_3$): δ = 163.30 – 160.11 (9 lines, 1F, J_{F-F} = 154.0 Hz), 140.56 (dm, 4F, J_{F-F} = 152.0 Hz), -31.23 (m, 1F).

Anal. Calcd for $C_{13}H_{13}F_6NOS$ (345.306): C, 45.22; H, 3.80; F, 33.01; N, 4.06.

Found: C, 45.30; H, 3.83; F, 33.12; N, 4.12.

3-Phenyl-5-(1-pentafluoro-λ^6-sulfanyl-2-chloroprop-3-yl)- 4,5-dihydroisoxazole (56).

According to the procedure for the synthesis of **52**.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.71 (m, 2H, Ar), 7.47 (m, 3H, Ar), 5.13 (m, 1H, OCH), 4.81 – 4.56 (m, 1H, ClCH), 4.29 - 3.98 (m, 2H, CH_2SF_5), 3.66 – 3.51 (dd, 1H, $J_{H,H}$ = 10.4 Hz, $J_{H,H}$ = 16.8 Hz, C*H*H), 3.15 – 3.00 (dd, 1H, $J_{H,H}$ = 8.0 Hz, $J_{H,H}$ = 16.8 Hz, CH*H*), 2.41 – 2.28 (m, 2H, CH_2) (a mixture of diastereomers).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 156.68, 156.58 (s, C=N), 130.43, 130.40 (s, CH, Ar), 129.14, 129.09 (s, C, Ar), 128.84, 128.82 (s, CH, Ar), 126.72 (s, CH, Ar), 77.40, 77.18 (s, OCH), 76.64, 76.60 (d pent, $J_{C,F}$ = 13.7 Hz, $J_{C,F}$ = 1.5 Hz, F_5SCH_2), 52.84, 52.60 (pent, $J_{C,F}$ = 4.5 Hz, CHCl), 43.32, 42.13 (pent, $J_{C,F}$ = 1.3 Hz, CH_2), 40.51, 40.21 (s, CH_2) (a mixture of diastereomers).

^{19}F NMR (188.3 MHz, $CDCl_3$): δ = 162.86 – 159.40 (18 lines, 1F, J_{F-F} = 146.0, 148.5 Hz), 144.96, 144.13 (dm, 4F, J_{F-F} = 146.0, 148.5 Hz), (a mixture of diastereomers).

Anal. Calcd for $C_{12}H_{13}ClF_5NOS$ (349.750): C, 41.21; H, 3.75; F, 27.16; N, 4.01.

Found: C, 41.29; H, 3.79; F, 27,28; N, 4.09.

3-(4-Fluorophenyl)-5-(1-pentafluoro-λ^6-sulfanyl-2-chloroprop-3-yl)- 4,5-dihydroisoxazole (57).

According to the procedure for the synthesis of **52**.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.70 (m, 2H, Ar), 7.15 (m, 2H, Ar), 5.19 – 5.09 (m, 1H, OCH), 4.78 – 4.58 (m, 1H, ClCH), 4.25 – 4.01 (m, 2H, CH_2SF_5), 3.66 – 3.51 (dd, 1H, $J_{H,H}$ = 10.2 Hz, $J_{H,H}$ = 16.6 Hz, C*H*H), 3.13 – 2.99 (dd, 1H, $J_{H,H}$ = 8.0 Hz, $J_{H,H}$ = 16.6 Hz, CH*H*), 2.32 (m, 2H, CH_2) (a mixture of diastereomers).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 163.88 (d, $J_{C,F}$ = 251.0 Hz, CF, Ar), 155.75, 155.66 (d, $J_{C,F}$ = 1.0 Hz C=N), 128.76, 128.60 (d, $J_{C,F}$ = 8.0 Hz, CH, Ar), 125.46, 125.44 (d, $J_{C,F}$ = 3.5 Hz, C, Ar), 116.15, 115.73 (d, $J_{C,F}$ = 22.1 Hz, CH, Ar), 77.57, 77.34 (s, OCH), 76.61, 76.55 (pent, $J_{C,F}$ = 13.9 Hz, F_5SCH_2), 52.81, 52.55 (pent, $J_{C,F}$ = 4.5 Hz, ClCH), 43.24, 42.06 (s, CH_2), 40.52, 40.23 (s, CH_2) (a mixture of diastereomers).

^{19}F NMR (188.3 MHz, $CDCl_3$): δ = 161.82 – 159.94 (18 lines, 1F, J_{F-F} = 144.0, 146.0 Hz), 144.69, 143.96 (dm, 4F, J_{F-F} = 144.0, 146.0 Hz), -32.84 (m, 1F). (a mixture of diastereomers).

Anal. Calcd for $C_{12}H_{12}ClF_6NOS$ (367.740): C, 39.19; H, 3.29; F, 31.00; N, 3.81.

Found: C, 39.10; H, 3.22; F, 31.12; N, 3.88.

3-Phenyl-5-(1-pentafluoro-λ^6-sulfanyl-2-chlorobut-4-yl)- 4,5-dihydroisoxazole (58).

According to the procedure for the synthesis of **52**.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.70 (m, 2H, Ar), 7.45 (m, 3H, Ar), 4.80 (m, 1H, OCH), 4.60 (m, 1H, ClCH), 4.01 (m, 2H, CH_2SF_5), 3.49 (dd, 1H, $J_{H,H}$ = 10.4 Hz, $J_{H,H}$ = 16.6 Hz, C*H*H), 3.06 (dd, 1H, $J_{H,H}$ = 7.6 Hz, $J_{H,H}$ = 16.6 Hz, CH*H*), 2.11 – 1.85 (m, 4H, $2CH_2$), (a mixture of diastereomers).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 156.53 (s, C=N), 130.20 (s, CH, Ar), 129.43 (s, C, Ar), 128.78 (s, CH, Ar), 126.64 (s, CH, Ar), 80.46, 79.68 (s, OCH), 76.71, 76.50 (d pent, $J_{C,F}$ = 13.4 Hz, $J_{C,F}$ = 0.8 Hz, F_5SCH_2), 55.77, 53.34 (pent, $J_{C,F}$ = 4.0 Hz, CHCl), 40.26, 40.08 (s, CH_2), 33.94, 33.23 (pent, $J_{C,F}$ = 1.3 Hz, *C*H_2-CHCl), 32.25, 31.72 (s, CH_2).

^{19}F NMR (188.3 MHz, $CDCl_3$): δ = 162.55 – 159.44 (9 lines, 1F, J_{F-F} = 146.4, 148.5 Hz), 144.13 (dm, 4F, J_{F-F} = 146.4 Hz), (a mixture of diastereomers).

Anal. Calcd for $C_{13}H_{15}ClF_5NOS$ (363.777): C, 42.92; H, 4.16; F, 26.11; N, 3.85.

Found: C, 42.80; H, 4.20; F, 26.23; N, 3.77.

3-(4-Fluorophenyl)-5-(1-pentafluoro-λ^6-sulfanyl-2-chlorobut-4-yl)- 4,5-dihydroisoxazole (59).

According to the procedure for the synthesis of **52**.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.67 (m, 2H, Ar), 7.11 (m, 2H, Ar), 4.79 (m, 1H, OCH), 4.45 (m, 1H, ClCH), 4.06 (m, 2H, CH_2SF_5), 3.46 (dd, 1H, $J_{H,H}$ = 10.4 Hz, $J_{H,H}$ = 16.6 Hz, C*H*H), 3.02 (dd, 1H, $J_{H,H}$ = 8.0 Hz, $J_{H,H}$ = 16.6 Hz, CH*H*), 2.10 – 1.83 (m, 4H, $2CH_2$) (a mixture of diastereomers).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 163.52 (d, $J_{C,F}$ = 251.0 Hz, CF, Ar), 155.37, 155.35 (d, $J_{C,F}$ = 1.0 Hz, C=N), 128.36 (d, $J_{C,F}$ = 8.1 Hz, CH, Ar), 125.55 (d, $J_{C,F}$ = 3.5 Hz, C, Ar), 115.60 (d, $J_{C,F}$ = 22.1 Hz, CH, Ar), 77.57, 77.34 (s, OCH), 76.61, 76.55 (pent, $J_{C,F}$ = 13.9 Hz, F_5SCH_2), 52.81, 52.55 (pent, $J_{C,F}$ = 4.5 Hz, ClCH), 43.24, 42.06 (s, CH_2), 40.52, 40.23 (s, CH_2).

^{19}F NMR (188.3 MHz, $CDCl_3$): δ = 161.43 – 159.57 (18 lines, 1F, J_{F-F} = 144.7, 146.0 Hz), 144.65, 143.56 (dm, 4F, J_{F-F} = 144.7, 146.0 Hz),, -31.44 (m, 1F). (a mixture of diastereomers).

(a mixture of diastereomers).

Anal. Calcd for $C_{13}H_{14}ClF_6NOS$ (381.767): C, 40.90; H, 3.70; F, 29.86; N, 3.67.

Found: C, 40.79; H, 3.75; F, 28.80; N, 3.70.

3-Acetyl-5-(1-pentafluoro-λ^6-sulfanylbut-1-en-3-yl)-4,5-dihydroisoxazole (60).

A mixture of 1-pentafluorosulfanylbut-1,3-diene **5 (**0.181 g, 0.001 mol) and ammonium cerium (IV) nitrate (0.558 g, 0.001 mol) in acetone (5mL) was stirred under reflux for 5 h. The mixture was extracted with ether (3x10) and washed with aq. Sodium hydrogencarbonate solution (2x5 mL), saturated aq. NaCl (2x5 mL). The ether solution was dried over Na_2SO_4 and concentrated in vacuum. The resulting oil was chromatographed on silica gel. Elution with chloroform gave 3-

acetyl-5-(1-pentafluorosulpanylbut-1-en-3-yl)-4,5-dihydroisoxazole **(60)** as a pale-yellow oil (0.214 g, 80%).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 6.62 (m, 2H, CH=CH), 5.10 – 4.92 (m, 1H, OCH), 3.16 (dd, 1H, $J_{H,H}$ = 11.0 Hz, $J_{H,H}$ = 17.0 Hz, C*H*H), 2.82 (dd, 1H, $J_{H,H}$ = 7.6 Hz, $J_{H,H}$ = 17.0 Hz, CH*H*), 2.55 (s, 3H, CH_3).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 193.10 (s, C=O), 158.30 (s, C=N), 143.80 (d.pent, $J_{C,F}$ = 20.2 Hz, $J_{C,F}$ = 1.6 Hz, =$CHSF_5$), 133.22 (pent, $J_{C,F}$ = 7.6 Hz, *C*H=$CHSF_5$), 81.96 (s, OCH), 36.94 (s, CH_2), 26.90 (s, CH_3).

^{19}F NMR (188.3 MHz, $CDCl_3$): δ = 162.23 – 159.04 (9 lines, 1F, J_{F-F} = 148.52 Hz), 140.11 (dm, 4F, J_{F-F} = 148.52 Hz).

Anal. Calcd for $C_7H_8F_5NO_2S$ (262.228): C, 32.06; H, 3.05; F, 36.26; N, 5.33.

Found: C, 32.21; H, 3.00; F, 36.10; N, 5.30.

3-Acetyl-5-(1-pentafluoro-λ^6-sulfanylprop-1-en-3-yl)-4,5-dihydroisoxazole (61).

A mixture of 1-pentafluorosulfanylpenta-1,4-diene **5 (**0.194 g, 0.001 mol) and ammonium cerium (IV) nitrate (0.558 g, 0.001 mol) in acetone (5mL) was stirred under reflux for 5 h. The mixture was extracted with ether (3x10) and washed with aq. Sodium hydrogencarbonate solution (2x5 mL), saturated aq. NaCl (2x5 mL). The ether solution was dried over Na_2SO_4 and concentrated in vacuum. The resulting oil was chromatographed on silica gel. Elution with chloroform gave 3-acetyl-5-(1-pentafluorosulpanylprop-1-en-3-yl)- 4,5-dihydroisoxazole **(61)** as a pale-yellow oil (0.215 g, 82%).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 6.52 (m, 2H, CH=CH), 5.04 – 4.90 (m, 1H, OCH), 3.15 (dd, 1H, $J_{H,H}$ = 11.0 Hz, $J_{H,H}$ = 17.6 Hz, C*H*H), 2.81 (dd, 1H, $J_{H,H}$ = 7.6 Hz, $J_{H,H}$ = 17.6 Hz, CH*H*), 2.54 (m, 2H, CH_2),2.52 (s, 3H, CH_3).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 193.10 (s, C=O), 158.30 (s, C=N), 143.80 (d.pent, $J_{C,F}$ = 20.2 Hz, $J_{C,F}$ = 1.6 Hz, =$CHSF_5$), 133.22 (pent, $J_{C,F}$ = 7.6 Hz, *C*H=$CHSF_5$), 81.96 (s, OCH), 36.94 (s, CH_2), 36.13 (s, CH_2), 26.96 (s, CH_3).

^{19}F NMR (188.3 MHz, $CDCl_3$): δ = 162.23 – 159.04 (9 lines, 1F, J_{F-F} = 148.52 Hz), 140.11 (dm, 4F, J_{F-F} = 148.52 Hz).

Anal. Calcd for $C_8H_{10}F_5NO_2S$ (279.228): C, 34.41; H, 3.61; F, 34.02; N, 5.02.

Found: C, 34.51; H, 3.67; F, 34.10; N, 5.14.

3-Acetyl-5-(1-pentafluoro-λ^6-sulfanylbut-1-en-4-yl)-4,5-dihydroisoxazole (62).

According to the procedure for the synthesis of **61**.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 6.51 (m, 2H, CH=CH), 4.89 – 4.73 (m, 1H, OCH), 3.22 (dd, 1H, $J_{H,H}$ = 10.8 Hz, $J_{H,H}$ = 17.4 Hz, C*H*H), 2.81 (dd, 1H, $J_{H,H}$ = 8.2 Hz, $J_{H,H}$ = 17.4 Hz, CH*H*), 2.51 (s, 3H, CH_3), 2.42 – 2.29 (m, 2H, CH_2), 1.95 – 1.77 (m, 2H, CH_2).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 193.37 (s, C=O), 158.53 (s, C=N), 141.71 (d.pent, $J_{C,F}$ = 29.6 Hz, $J_{C,F}$ = 2.0 Hz, =CHSF$_5$), 137.82 (pent, $J_{C,F}$ = 7.5 Hz, *C*H=CHSF$_5$), 83.42 (s, OCH), 37.35 (s, CH_2), 33.37 (s, CH_2), 26.95 (s, CH_2), 26.83 (s, CH_3).

^{19}F NMR (188.3 MHz, $CDCl_3$): δ = 163.15 – 159.96 (9 lines, 1F, J_{F-F} = 148.50 Hz), 140.48 (dm, 4F, J_{F-F} = 148.50 Hz),

Anal. Calcd for $C_9H_{12}F_5NO_2S$ (293.255): C, 36.86; H, 4.12; F, 32.39; N, 4.78.

Found: C, 36.96; H, 4.62; F, 32.52; N, 4.88.

3-Acetyl-5-(1-pentafluoro-λ^6-sulfanyl-2-chloroprop-3-yl)-4,5-dihydroisoxazole (63).

According to the procedure for the synthesis of **61**.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.29 – 5.08 (m, 1H, OCH), 4.78 – 4.46 (m, 1H, ClCH), 4.22 – 3.89 (m, 2H, CH_2SF_5), 3.35 (dd, 1H, $J_{H,H}$ = 10.2 Hz, $J_{H,H}$ = 17.0 Hz, C*H*H), 2.82 (dd, 1H, $J_{H,H}$ = 7.6 Hz, $J_{H,H}$ = 17.0 Hz, CH*H*), 2.52 (s, 3H, CH_3), 2.40 – 1.84 (m, 2H, CH_2) (a mixture of diastereomers).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 193.31, 193.23 (s, C=O), 158.61, 158.42 (s, C=N), 80.99, 80.61 (s, OCH), 76.84, 76.77 (pent, $J_{C,F}$ = 13.0 Hz, F_5SCH_2), 52.68, 52.59 (pent, $J_{C,F}$ = 4.5 Hz, CHCl), 43.57, 42.25 (s, *C*H_2-CHCl), 37.90, 37.58 (s, CH_2), 27.14, 27.11 (s, CH_3) (a mixture of diastereomers).

^{19}F NMR (188.3 MHz, $CDCl_3$): δ = 161.44 – 159.63 (18 lines, 1F, J_{F-F} = 146.6, 148.0 Hz), 144.65, 144.03 (dm, 4F, J_{F-F} = 146.6, 148.0 Hz), (a mixture of diastereomers).

Anal. Calcd for $C_8H_{11}ClF_5NO_2S$ (315.689): C, 30.44; H, 3.51; F, 30.09; N, 4.44.

Found: C, 30.57; H, 3.55; F, 30.12; N, 4.50.

3-Acetyl-5-(1-pentafluoro-λ^6-sulfanyl-2-chlorobut-3-yl)-4,5-dihydroisoxazole (64).

According to the procedure for the synthesis of **61**.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.94 – 4.79 (m, 1H, OCH), 4.50 – 4.37 (m, 1H, ClCH), 4.18 – 3.85 (m, 2H, CH_2SF_5), 3.26 (dd, 1H, $J_{H,H}$ = 10.4 Hz, $J_{H,H}$ = 16.8 Hz, C*H*H), 2.86 (dd, 1H, $J_{H,H}$ = 8.0 Hz, $J_{H,H}$ = 16.8 Hz, CH*H*), 2.52 (s, 3H, CH_3), 2.10 – 1.80 (m, 4H, CH_2) (a mixture of diastereomers).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 193.48, 193.46 (s, C=O), 158.58, 158.56 (s, C=N), 84.07, 83.36 (s, OCH), 76.84, 76.86 (pent, $J_{C,F}$ = 15.4 Hz, F_5SCH_2), 55.84, 55.46 (pent, $J_{C,F}$ = 4.5 Hz, CHCl), 37.59, 37.63 (s, CH_2), 34.04, 33.40 (s, CH_2), 32.49, 32.06 (s, CH_2), 27.0 (s, CH_3).

^{19}F NMR (188.3 MHz, $CDCl_3$): δ = 161.54 – 159.74 (18 lines, 1F, J_{F-F} = 146.0, 148.0 Hz), 144.75, 144.34 (dm, 4F, J_{F-F} = 146.0, 148.0 Hz), (a mixture of diastereomers).

Anal. Calcd for $C_9H_{13}ClF_5NO_2S$ (327.700): C, 32.99; H, 3.38; F, 28.99; N, 4.27.

Found: C, 32.87; H, 3.47; F, 28.84; N, 4.39.

1-(Pentafluoro-λ^6-sulfanyl)prop-1-enyl ether 3-amino-4-carboxyfurazan (65).

1-(Pentafluoro-λ^6-sulfanyl)prop-1-en-3-ol (**26**) (0.22 g, 0.0012 mol), 3-amino-4-carboxyfurazan (0.129 g, 0.001 mol) and DMAP (0.125 g, 0.001 mol) were dissolved in 10 mL of $CH_3OCH_2CH_2OCH_3$ and then 0.2 g (0/001 mol) of DCC in 5 mL of $CH_3OCH_2CH_2OCH_3$ was added. After the solution was stirred at rt overnight and the reaction mixture was concentrated. The crude product was purified by column chromatography using chloroform/methanol (10/0.5), to give 0.19 g of the target ether (**65**) in 65% yield.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 6.82 – 6.63 (m, 2H, CH=CH), 5.17 (br. s, 2H, NH_2), 5.11 (m, 2H, CH_2).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 159.38 (s, =C, furazan), 156.46 (s, =C, furazan), 143.30 (d pent, $J_{C,F}$ = 2.0 Hz, $J_{C,F}$ = 21.7 Hz, F_5SCH=), 138.28 (s, C=O), 131.39 (pent, $J_{C,F}$ = 7.5 Hz, =CH), 65.82 (s, CH_2).

^{19}F NMR (188.3 MHz, $CDCl_3$): δ = 161.06 – 157.85 (9 lines, 1F, J_{F-F} = 150.4 Hz), 140.59 (dm, 4F, J_{F-F} = 150.4 Hz).

Anal. Calcd for $C_6H_6F_5N_3O_3S$ (315.0): C, 22.86; H, 1.90; F, 30.16; N, 13.33.

Found: C, 22.98; H, 1.95; F, 30.32; N, 1348.

1-(Pentafluoro-λ^6-sulfanyl)-1,1,2,2-tetrafluoropropyl ether of 3-amino-4-carboxyfurazan (66).

According to the procedure for the synthesis of **65**.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.37 (br. s, 2H, NH_2).

^{19}F NMR (188 MHz, $CDCl_3$): δ = 144.0 (9 lines, 1F, $J_{F,F}$ = 142.0 Hz, 1 F), 135.43 (d m, 4F $J_{F,F}$ = 142.0 Hz, 4 F), -18.23 (m, 2F, $J_{F,F}$ = 11.0 Hz, $J_{F,F}$ = 18.8 Hz, CF_2), -41.89 (m, 2F, $J_{F,F}$ = 18.8 Hz).

Anal. Calcd for $C_6H_4F_9N_3O_3S$ (373.0): C, 19.30; F 45.84. Found: C, 19.47; S 45.72.

1,4-Dibenzoxybut-2,3-dion (68)

A mixture of dichloromethane (100 mL), acetic acid (5 mL) and **67** (4.2g, 0.014 mol) is stirred and heated to reflux temperature before powder potassium permanganate (5.85 g, 0.037 mol) and phase-transfer agent (Adogen-464; 1.6 g) are added. After bring stirred vigorously for 4 h the precipitated manganese dioxide is collected and washed with dichloromethane (2x50 mL). Residual manganese dioxide is reduced by addition (to the combined filtrates) of 20% hydrochloric acid (40 mL) followed by small portions of sodium hydrogen sulfite until all of the brown color has disappeared. The organic phase is separated, washed with water, and dried with $MgSO_4$. The solvent was removed and the remaining oil distilled under vacuum to give 2.52 g (60%) **68**; b.p. 142-145 (0.5 mm Hg).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.37 (m, 10H, 2 C_6H_5), 4.71 (s, 4H, 2$\underline{CH_2}$Ph), 4,62 (s, 4H, 2CH_2C(O)).

1,4-Dibenzoxybut-2,3-dioxime (69)

A mixture of 7.45 g (0.025 mol) of 1,4-dibenzoxybut-2,3-dion **(68)**, 11.40 g (0.165 mol) of hydroxylamine hydrochloride, and 22.6 g (0.165 mol) of sodium acetate trihydrate in 200 mL of absolute ethanol was refluxed for 45 min, and then *ca.* 50 mL of ethanol was remobed at 25^0 (25 mm Hg). The residue was added to 100 mL of ace water and the product was extracted with 35 mL of methylene chloride. The extract was dried and concentrated to leave 5.5 g of oil. The crude product was purified by column chromatography using chloroform/methanol (10/01.5), to give 3.5 g of the target dioxime (**69**) in 46% yield as mixture of isomers.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.38 (m, 10H, 2 C_6H_5), 4.70 (s, 4H, 2$\underline{CH_2}$Ph), 4,43(s, 4H, 2CH_2C(O)), 2.6 (br.s., 2H, 2 OH).

3,4-Dibenzoxymethylfurazane (70)

A mixture of 1,4-dibenzoxybut-2,3-dioxime **(69)** (6.6g, 0.02 mol) and aqueous sodium hydroxide (0.8 g in 10 mL of water) in a closed stainless steel reactor was heated in an oil bath for 2 h at 170-180^{0}C. The reactor was cooled in an ice-bath and opened. A precipitate was isolated, washed with cold water (3x10 ml), and dried to give 3,4-dibenzoxymethylfurazane **(70)** as colorless needles, 5 g (50%), mp 143-150^{0}C.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.38 (m, 10H, 2 C_6H_5), 4.70 (s, 4H, 2$\underline{CH_2}$Ph), 4,65(s, 4H, 2CH_2C=).

3,4-Dihydroxymethylfurazan (71).

A solution of compound 3,4-dibenzoxymethylfurazane **(70)** (2.78 g, 0.01 mmol) in methanol (20 mL) was hydrogenated over 5% Pd/C (0.03 g) at atmospheric pressure. The mixture was vigorously stirred at room temperature for 1 h, whereupon the catalyst was removed by filtration and the filtrate concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel; CH_2Cl_2/MeOH, 10:2) to give **171** (0.91 g, 96%) as white solid, (m.p. 74-78 ^{o}C).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.38 (m, 10H, 2 C_6H_5), 4,67(s, 4H, 2CH_2C=), 3.2 (br.s., 2H, 2OH).

Reaction 3,4-dioxymethylfurazan with 3-(Pentafluoro-λ^6-sulfanyl)prop-2-enoic acid (72)

3-(Pentafluoro-λ^6-sulfanyl)prop-2-enoic acid (**28**) (0.594 g, 0.003 mol), 2,4-dioxymethylfurazan (0.13 g, 0.001 mol) and DMAP (0.25 g, 0.002 mol) were dissolved in 15 mL of $CH_3OCH_2CH_2OCH_3$ and then 0.4 g (0.002 mol) of DCC in 5 mL of $CH_3OCH_2CH_2OCH_3$ was added. After the solution was stirred at rt overnight and the reaction mixture was concentrated. The crude product was purified by column chromatography using chloroform/methanol (10/0.2), to give 0.22 g of the target diether (**72**) in 45% yield.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.55 (d pent, 2 H, J_{H-H} = 15.0 Hz, J_{H-F} = 7.0 Hz, 2 =$CHSF_5$), 6.66 (d pent, 2 H, J_{H-H} = 15.0 Hz, J_{H-F} = 1.2 Hz, 2 =CHCOO), 4.53 (s, 4H, 2CH_2).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 168.57 (s, C=O), 154.50 (d pent, J_{C-F} = 1.5 Hz, J_{C-F} = 20.4 Hz, =$CHSF_5$), 154.45 (s, =C, furazan), 131.39 (pent, $J_{C,F}$ = 7.5 Hz, =CH), 68.82 (s, CH_2).

^{19}F NMR (188.3 MHz, $CDCl_3$): δ = 161.22 – 1567.05 (9 lines, 1F, J_{F-F} = 150.0 Hz), 141.00 (dm, 4F, J_{F-F} = 150.0 Hz).

Anal. Calcd for $C_{10}H_8F_{10}N_2O_5S_2$ (490.0): C, 24.49; H, 1.63; N, 8.57.

Found: C, 24.69; H, 1.60; 16; N, 8.69.

Reaction 3,4-dioxymethylfurazan with 3-(Pentafluoro-λ^6-sulfanyl)-2-chloropropionic acid (73)

3-(Pentafluoro-λ^6-sulfanyl)-2-chloropropionic acid (**31**) (0.7 g, 0.003 mol), 2,4-dioxymethylfurazan (0.13 g, 0.001 mol) and DMAP (0.25 g, 0.002 mol) were dissolved in 15 mL of $CH_3OCH_2CH_2OCH_3$ and then 0.4 g (0.002 mol) of DCC in 5 mL of $CH_3OCH_2CH_2OCH_3$ was added. After the solution was stirred at rt overnight and the reaction mixture was concentrated. The crude product was purified by column chromatography using chloroform/methanol (10/0.2), to give 0.16 g of the target diether (**73**) in 28% yield.

^{1}NMR (200 MHz, $CDCl_3$): δ = 4.86 (dd, 2H, J_{H-H} = 10.0 Hz, J_{H-H} = 4.0 Hz, 2CHCl), 4.65 (dd pent, 2 H, J_{H-H} = 10.0 Hz, J_{H-H} = 16.6 Hz, J_{H-F} = 7.4 Hz, 2C*H*HSF$_5$), 4.05 (dd pent, 2 H, J_{H-H} = 3.8 Hz, J_{H-H} = 16.6 Hz, J_{H-F} = 7.4 Hz, 2C*H*HSF$_5$).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 171.62 (s, C=O), 154.45 (s, =C, furazan), 71.75 (pent, J_{C-F} = 18.6 Hz, CH_2SF_5), 68.82 (s, CH_2), 50.10 (pent, J_{C-F} = 6.0 Hz, HCCl).

^{19}F NMR (188 MHz, $CDCl_3$): δ = 156.82 (9 lines, $J_{F,F}$ = 145.9 Hz, 1 F), 144.40 (d m, $J_{F,F}$ = 145.9 Hz, 4 F).

Anal. Calcd for $C_{10}H_{10}Cl_2F_{10}N_2O_5S_2$ (562.0): C, 21.35; H, 1.78; N, 4.45.

Found: C, 21.45; H, 1.93; 16; N, 4.60.

Reaction 3,4-dioxymethylfurazan with 3-(Pentafluoro-λ^6-sulfanyl)-3,3,2,2-tetrafluoro-propionic acid (74)

3-(Pentafluoro-λ^6-sulfanyl)-3,3,2,2-tetrafluoropropionic acid (**51**) (0.816 g, 0.003 mol), 2,4-dioxymethylfurazan (0.13 g, 0.001 mol) and DMAP (0.25 g, 0.002 mol) were dissolved in 15 mL of $CH_3OCH_2CH_2OCH_3$ and then 0.4 g (0.002 mol) of DCC in 5 mL of $CH_3OCH_2CH_2OCH_3$ was added. After the solution was stirred at rt overnight and the reaction mixture was concentrated. The crude product was purified by column chromatography using chloroform/methanol (10/0.2), to give 0.26 g of the target diether (**74**) in 40% yield.

^{19}F NMR (188 MHz, $CDCl_3$): δ = 148.0 (9 lines, 1F, $J_{F,F}$ = 149.0 Hz, 1 F), 134.60 (d m, 4F $J_{F,F}$ = 142.0 Hz, 4 F), -19.43 (m, 2F, $J_{F,F}$ = 12.0 Hz, $J_{F,F}$ = 17.0 Hz, CF_2), -40.42 (m, 2F, $J_{F,F}$ = 17.0 Hz).

Anal. Calcd for $C_{10}H_4F_{18}N_2O_5S_2$ (638.0): C, 18.81; S 10.03.76. Found: C, 18.92; S 10.21.

3-Chloro-1-(pentafluoro-λ^6-sulfanyl)prop-1-en (75)

A mixture of 1-pentafluorosulfanylpen-1-en-3ol **(26) (**9.2 g, 0.05 mol), 8.9 g (0.075 mol) of $SOCl_2$ and 2 mL of pyridine was stirred under reflux for 3 h and then surplus was removed. The residue was added to 20 mL of cold water and the product was extracted with 3x10 mL of methylene chloride. The extract was dried and concentrated. The crude product was purification by distillation. B.p. 132-133^{0}C. Yield 6.3g (62%).

^{1}H NMR ($CDCl_3$): δ = 4.18 – 4.21 (m, 2H), 6.51 – 6.86 (m, 2H); ^{13}C NMR ($CDCl_3$): δ = 40.95 (s), 133.0 (pent, J_{C-F} = 7.4 Hz), 143.55 (d pent, J_{C-F} = 1.6 Hz, J_{C-F} = 21.3 Hz).

^{19}F NMR ($CDCl_3$): δ = 140.56 (m, incl. app. d, J_{F-F} = 148.0 Hz, 4F), 157.67 – 160.86 (m, 1F). Elemental analysis: % calculated for $C_3H_4ClF_5S$: C, 17.79; H, 1.99; S, 15.83; found: C, 17.94; H, 2.07; S, 15.67.

3-azido-1-(pentafluoro-λ^6-sulfanyl)prop-1-en (76)

A mixture of 3-chloro-1-(pentafluoro-λ^6-sulfanyl)prop-1-en **(75) (**1.01 g, 0.005 mol) and NaN_3 (1.0 g, 0.015 mol) in MeOH (10 mL) was stirred at 40-50^{0}C for 5 h. The reaction mixture is then quenched by adding 50 mL of H_2O and extracted with ether (3x10). The ether solution was dried over Na_2SO_4 and concentrated in vacuum. The resulting oil was chromatographed on silica gel. Flash chromatography with chloroform gives **76** (0.82 g, 78%).

^{1}H NMR ($CDCl_3$): δ = 4.09 (d pent, J_{H-H} = 2.4 Hz, J_{H-H} = 2.0 Hz, 2H), 6.47 – 6.59 (m, 1H), 6.74 (d pent t, J_{H-H} = 8.4 Hz, J_{H-F} = 6.2 Hz, J_{H-H} = 1.8 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ = 49.97(s), 132.71 (pent, J_{C-F} = 7.1 Hz), 142.90 (d pent, J_{C-F} = 1.7 Hz, J_{C-F} = 21.3 Hz).

^{19}F NMR ($CDCl_3$): δ = 140.39 (m, incl. app. d, J_{F-F} = 150.5 Hz, 4F), 157.94 – 161.13 (m, 1F). Elemental analysis: % calculated for $C_3H_4F_5N_3S$: C, 17.23; H, 1.93; S, 15.32; found: C, 17.48; H, 2.12; S, 15.60.

1-(pentafluoro-λ^6-sulfanyl)prop-1-enyl thiocyanate (77)

According to the procedure for the synthesis of **61**.

^{1}H NMR ($CDCl_3$): δ = 3.65 – 3.66 (m, 1H), 3.67 – 3.69 (m, 1H), 6.54 – 6.86 (m, 2H); ^{13}C NMR ($CDCl_3$): δ = 33.24 (s), 110.49 (s), 131.41 (pent, J_{C-F} = 7.0 Hz), 145.12 (d pent, J_{C-F} = 1.5 Hz, J_{C-F} = 20.1 Hz).

^{19}F NMR ($CDCl_3$): δ = 140.51 (m, incl. app. d, J_{F-F} = 150.4 Hz, 4F), 156.61 – 159.81 (m, 1F). Elemental analysis: % calculated for $C_4H_4F_5NS_2$: C, 21.33; H, 1.79; S, 28.48; found: C, 21.47; H, 1.84; S, 28.56.

1-Chloro-3-(pentafluoro-λ^6-sulfanyl)prop-1-en (78)

A mixture of 3-chloro-1-(pentafluoro-λ^6-sulfanyl)prop-1-en **(75) (**1.01 g, 0.005 mol) and Cs_2CO_3 (0.05 g) in MeOH (10 mL) was stirred at rom temperature 24 h. The reaction mixture is then quenched by adding 50 mL of H_2O and extracted with ether (3x10). The ether solution was dried over Na_2SO_4 and concentrated in vacuum. The resulting oil was chromatographed on silica gel. Flash chromatography with chloroform gives **78** (0.91 g, 90%).

^{1}H NMR ($CDCl_3$): δ = 4.55 (d d pent, J_{H-H} = 7.2 Hz, J_{H-H} = 0.5 Hz, J_{H-F} = 7.6 Hz, 2H), 6.12 (d.t, J_{H-H} = 7.2 Hz, J_{H-H} = 7.6 Hz, 1H), 6.50 (d t, J_{H-H} = 7.2 Hz, J_{H-H} = 1.0 Hz, 1H).

^{13}C NMR ($CDCl_3$): δ = 67.05 (d pent, J_{C-F} = 1.0 Hz, J_{C-F} = 16.5 Hz), 120.91 (pent, J_{C-F} = 4.1 Hz), 126.58 (pent, J_{C-F} = 1.0 Hz); ^{19}F NMR ($CDCl_3$): δ = 143.72 (m, incl. app. d, J_{F-F} = 145.0 Hz, 4F), 157.50 – 161.23 (m, 1F). Elemental analysis: % calculated for $C_3H_4ClF_5S$: C, 17.79; H, 1.99; S, 15.83; found: C, 17.84; H, 2.05; S, 15.97.

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11. Conclusion.

1. We have developed a convenient method for preparation of organic compounds containing pentafluorosulfanyl substituent based on the photochemical addition of pentafluorosulfanyl chloride to different dienes and unsaturated alcohols.
2. For the first time, we have synthesized pentafluorosulfanyl-containing derivatives of 1,3-, 1,4-, and 1,5-dienes what are the promising monomers for the development of new polymer materials. It was shown that treatment with H_2O_2 leads to polymerization of 1-(pentafluorosulfanyl)-1,3-butadiene polymerizes with formation of some oligomers.
3. Epoxidation of alkenes and dienes containing pentafluorosulfanyl group by m-chloroperoxybenzoic acid (mCPBA) has been studied. It was found that F_5S group

deactivates double bond *vs* electrophilic reagents; double bonds connected directly to F_5S group are inert against mCPBA.

4. For the first time, we have synthesized active pentafluorosulfanyl-containing dienophiles using unsaturated alcohols as starting compounds. [2+4]-Cycloaddition reactions between these dienophiles and cyclopentadiene or electron-releasing acyclic 1,3-dienes have been studied. Factors controlling the efficiency of this kinf of cycloaddition have been determined. Some new promising norbornene-based monomers with F_5S group for preparation of transparent polymers for 157 nm technology have been synthesized. Investigation of their polymerization is in progress now.
5. Photo-induced radical addition of pentafluorosulfanyl chloride to esters of perfluoroacrylic acid has been studied. A new method of preparation of pentafluorosulfanyl-containing derivatives of perfluoropropionic acid has been developed.
6. Reactions of F_5S-substituted alkenes and dienes with nitrile oxides have been investigated. For the first time, convenient method of preparation of 4,5-dihydroisoxazoles with pentafluorosulfanyl substituent has been developed.
7. It was shown that 1-(pentafluorosulfanyl)-3-chloroprop-1-ene undergoes prototropic rearrangement in the presence of base.
8. During the project realization for the first time we have synthesized 64 new compounds with pentafluorosulfanyl group. The structures of all synthesized compounds have been proved by ^{1}H, ^{19}F, and ^{13}C spectroscopy data.

12. References

(1) Gard, G. L.; Woolf, C. W. *US Pat. 3 448 121*, **1969**. Gard, G. L.; Bach, J.; Woolf, C. W. *Br. Pat. 1 167 112*, **1969**. Gilbert, E. E.; Gard, G. L. *US Pat. 3 475 453*, **1969**. Banks, R. E.; Haszeldine, R. N. *Br. Pat. 1 145 263*, **1969**. Shepard, W. A. *US Pat. 3 219 690*, **1965**.

(2) Witucki, E. F.; Frankel, M.B. *J. Chem Tng. Data* **1979,** *24*, 382. Sitzmann, M. E.; Gilligan, W. H.; Ornellas, D. L.; Thrasher, J. S. *J. Energ. Mater.* **1990,** *8*, 352. Sitzmann, M. E. *J. Fluorine Chem.* **1991,** *52*, 195. Sitzmann, M. E.; Gilardi, R. D. *J. Fluorine Chem.* **1993,** 203.

(3) Bovin, J. L. *Can. Patent* 1,085,875 **1980**.

(4) Kostov, G.; Ameduri, B.; Sergeeva, T.; Dolbier, Jr.,W.R.; Winter, R; Gard, G.L. *Macromaleculas*, **2005**, A-K.

(5) (a) Kirsch, P.; Bremer, M.; Heckmeier, M.; Tarumi, K. *Angew. Chem. Ed.*, **199**, *38*, N13/4, 1989-1992. (b) Smoth, J.A.; DiStasio Jr. A.; Hannah, N.A.; Winter. R.W.; Weakly, T.J.R.; Gard, G.L.; Rananavare, S.B. *J. Phys. Chem. B*, **2004**, *108*, 19940.

(6) Case, J. R.; Ray, N. H.; Roberts, H. L. *J. Chem. Soc.* **1961**, 2066.

(7) Verma, R. D.; Kirchmeier, R. L.; Shreeve, J. M. In *Advances in Inorganic Chemistry*, Vol. 41; Sykes, A. G., Ed.; Academic Press: London, 1994, p 125. Winter, R.; Gard, G.L. In *Inorganic Fluorine Chemistry: Toward the 21st Century*, Chapter 8; Trasher, J. S., Strauss, S. H., Eds.; ACS Symposium Series 555, Washington, DC, 1994, p 128.

(8) Hudlicky, M. *Oxidation in Organic Chemistry*, American Chemical Society: Washington DC, 1990. Haines, A. H. *Methods for the Oxidation of Organic Compounds*, Academic Press: New York, 1985. Dryuk, V. G. *Russian Chem. Rev.* **1985**, *54*, 986.

(9) (a) Bloomstein, T.M.; Horn, M.W.; Rothaschild, M.; Kunz, R.R.; Palamacci, S.T.; Goodman, R.B.J. *Vac. Sci. Technol. B.* **1997**, *13*, 2112.(b) Kunz, R.R.; Bloomstein, T.M.; Hardy, D.E.; Goodman, R.B.J.; Downs, D.K.; Curtin, J.E. *Proc. SPIE*, **1999**, 3678, 12-13.

(11) Thomas, B.H.; Shafer, G.; DesMarteau, D.D.; Chiba, T.; Willson, G.; Conley, W.; Miller, D. *!3thEuropean Symposium on Fluorine Chemistry, Bordeaux, France, 2001, Abstracts Book, 1-P79.*

(12) Pattison, L. M.; Stothers, L. B.; Woolford, R. G. *J. Am. Chem. Soc.* **1959**, *78*, 2252.

(13) Winter, R.; Gard, G. L. *J. Fluorine Chem.* **2000**, *102*, 79.

(14) Winter, R.; Nixon, P. G.; Gard, G. L.; Rabford, D. H.; Holcomb, N. R.; Grainger, D. W. *J. Fluorine Chem* **2001**, *107*, 23.

(15) (a) Nixon, P. G.; Winter, R.; Catner, D.G.; Holcomb, N.R.; Grinder, D.W.; Gard, G.L. *Chem. Mater.*, **2000**, *12*, 3108-3112. (b) Winter, R.; Nixon, P. G.; Terjeson, R.S.; Mohtashum, J.; Holcomb, N.R.; Grinder, D.W.; Graham, D.; Castner, G.L.; Gard, G.L. *J. Fluorine Chem* **2002**, *115*, 107.

(16) Hansen, J.C.; Savn,P.M. *US Pat. 5 286 352*, **1994**.

(17) общая ссылка на изоксазолы

(18) Grundmann,C.; Grunanger, P. *Nitrile Oxides.* Berlin: Springer-Verlag, **1971**.

(19) Itoh, K-i.; Takahushi, S.; Ueki, T.; Sugiyama, T.; Tukuhushi, T.T.; Horiuchi, C.A. *Tetrahedron Letters*, **2002**, *43*, 7035.

(20) Sheremetev, A.B.; Makhova, N.N.; Friedrichsen, W.Y. *Adv. Heterocycl. Chem.*, ed. A.R.Katrizky, Academic Press, San Diego, **2001**, vol. 78, 65-188.

(21) Lee, D.G.; Chang, V.S. *Synthesis*, **1978**, 462.

(22) Grakauskas, V. *J. Org. Chem.*, **1973**, *58*, 2999.

(23) Gunasekaran, A.; Boyer, J.H. *Heteroatom Chemistry*, **1993**, *4*, 521.

(24) Smith, M. B.; March J. *March's Advanced Organic Chemistry. Reactions, Mechanisms, and Structure* 5th Ed., Wiley, 2000, 2083 pp.

(25) Bernasconi, C. F. *Acc. Chem. Res.* **1987**, 20, 301-308.

(26) Schack, C. J.; Wilson, R. D.; Warner, M. G. *Inorganic Synthesis*, Vol. 24; Shreeve, J. M., Ed.; John Wiley & Sons, Inc., New York, 1986, p 8.

13. List of published papers (with abstracts).

1) Brel, V.K. "Synthesis and epoxidation of 1,3-, 1,4-, 1,5-alkadienes with pentafluoro-λ^6-sulfanyl (SF_5) groupings" *Synthesis*, **2005**, 1245.

This paper describes a convenient and efficient synthesis of new pentafluoro-λ^6-sulfanyl-containing 1,3-, 1,4- and 1,5-alkadienes and studied their epoxidation. These compounds are useful as monomers or as intermediated in the preparation of polymers, polymer surface coating and F_5S containing heterocyclic compounds.

2) Trushkov, I.V.; Brel, V.K. "Unusual Reactivity of 3-chloro-1-Pentafluorosulfanylpropene in Nucleophilic Substitution Reactions Substitution Reactions" *Tetrahedron Letters*, **2005**, *46*, 4777.

Treatment of 3-chloro-1-pentafluorosulfanylprop-1-ene (**1**) with KCN yields unusually the product of prototropic rearrangement $ClCH{=}CHCH_2SF_5$ whereas reactions with NaN_3 and KSCN gave the common S_N2 products. The *ab initio* calculations at MP2/6-311++G** level have been used to explain the unusual behavior of cyanide. It is found that proton transfers from both **1** to CN^- and from HCN to anion of **1** are exothermic. Oppositely, azide and thiocyanate ions are too weak bases to deprotonate **1**.

14. List of presentations at conferences and meetings (with abstracts).

1) Brel, V.K. "ALKENES AND AZIDES WITH PENTAFLUORO-λ^6-SULFANYL (SF_5) GROUPINGS IN REACTIONS OF 1,3-DIPOLAR CYCLOADDITION". *IX Joint Meeting on Heterocyclic Chemistry* (May 05-09 2004, Urbino, Italy).

The introduction of pentafluorothio (SF_5, pentafluoro-λ^6-sulfanyl) groupings into molecular systems can bring about substantial changes with regard to their physical, chemical and biological behavior. Compounds in which this group is present are of special interest because they often possess the advantageous properties of the parent compound, SF_6, among which are a high group electronegativity, large steric bulk, a nonfunctional hexacoordinate stereochemistry, and high hydrolytic stability. In connection with our interest in chemistry of various organic compounds with electronegative groups, we have developed convenient approaches to synthesis of unsaturated compounds with pentafluorothio groups and used them for designing heterocyclic compounds. We have studied 1,3-dipol cycloaddition reactions of: 1-(pentafluoro-λ^6-sulfanyl)-1,3-butadiene, 1-(pentafluoro-λ^6-sulfanyl)-1,4-pentadiene, 1-(pentafluoro-λ^6-sulfanyl)-1,5-hexadiene with nitrile oxides, and 1-(pentafluoro-λ^6-sulfanyl)-3-azide-1-propen with acetylenes.

2) Brel, V.K "APPROACHES TO SYNTHESIS OF UNSATURATED COMPOUNDS WITH PENTAFLUORO-λ^6-SULFANYL (SF_5) TERMINAL GROUPINGS."10th Belgian Organic Synthesis Symposium (July 12-16, 2004, Louvain-la-Neuve, Belgium)

As part of a program concerned with the synthesis and characterization of new pentafluorosulfur derivatives, we became interested in the development of synthetic approaches to various unsaturated compounds with pentafluoro-λ^6-sulfanyl terminal groupings. We have found that the new SF_5-containing alkadienes, alcohols, azide, ketone, chlorides can be prepared using the appropriate unsaturated precursor via the following pathways. Structure compounds were identified by ^1H, ^{13}C, ^{19}F and MS spectral data.

3) Brel, V.K **"DEVELOPMENT OF SYNTHETIC APPROACHES TO POLYFUNCTIONAL COMPOUNDS WITH PENTAFLUOROSULFANYL (SF_5) GROUPING".** 1st International Symposium on Fluorous Technologies, July 3-6, 2005, Bordeaux, France.

Sulfur chloride pentafluoride (F_5SCl) has been utilized in reactions with variety of unsaturated compounds. We have investigated the development of some novel reaction systems with (F_5SCl). Using the reaction between the sulfur chloride pentafluoride (F_5SCl) and unsaturated alcohols or

1,4-, 1,5-alkadienes (in gas phase) under irradiation of ultra-violet light leads to products of addition of F_5SCl to the double bounds in good yields. These adducts were used as useful precursors for preparation of new unsaturated, cyclyc and heterocyclic compounds with pentafluorothio groups. The structure of synthesized new compounds, were characterized by ^{1}H, ^{13}C, and ^{31}P NMR data and in some cases by single crystal X-ray crystallography. The details of the synthesis, spectroscopic properties and X-ray data will be discussed.

4) Brel, V.K **"DEVELOPMENT OF SYNTHETIC APPROACHES TO POLYFUNCTIONAL COMPOUNDS WITH PENTAFLUOROSULFANYL (SF_5) GROUPING". 20**th International Congress of Heterocyclic Chemistry, July 31 – August 5, 2005, Palermo, Italy.

We have studied reactivity of unsaturated pentafluorosulfanyl derivatives as dipolarophiles in 1,3-dipolar cycloaddition. Reactions of 1,3-dipolar cycloaddition between 1,3-, 1,4- and 1,5-alkadienes with pentafluorothio group (F_5S) and arylnitrile oxides were performed in diethyl ether at -20^0C. Compounds 1,4- and 1,5-alkadienes with pentafluorothio group reacts smoothly with benzonitrile oxides providing isoxazolines with good yields. On the contrary, 1- pentafluorosulfanylbuta-1,3-diene does not react with nitrile oxides and CAN(IV) in acetone.